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THE CHEMICAL NEWS, JULY 3, 1896.

THE
CHEMICAL NEWS

AND
JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

WILLIAM CROOKES, F.R.S., &c.

VOLUME LXXIII.—1896.

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THE CHEMICAL NEWS.

VOLUME LXXIII.

EDITED BY WILLIAM CROOKES, F.R.S., &c.

No. 1884.—JANUARY 3, 1896.

NOTE ON THE ANALYSIS OF CHROME-IRON ORE, FERRO- CHROMIUM, AND CHROME STEEL.

By Dr. S. RIDEAL and S. ROSENBLUM.

ABOUT 1820 chrome ores were first introduced in considerable quantities for the manufacture of chromium salts, and naturally the quantitative determination of the amount of metallic chromium contained in them received much attention at the hands of chemists.

Calvert 1852 (1), Bunsen 1854 (2), and Woehler (4) some years later were the first to devise satisfactory quantitative methods for the analysis of chrome ores, but these methods were very incomplete and would hardly satisfy the modern chemist.

Since then chromium has taken a very prominent place in chemical industry, and the literature referring to the determination of it has increased in proportion to its use in the production of various salts, chrome paints, ferro-chromium, chrome-steel, &c.

The list of papers on this subject which we have selected, and which, as regards the analysis of chrome-steel, is still far from being complete, will give some idea of the importance of the subject and of the number of eminent chemists who have made a special study of it.

In the proposals which have been made for the quantitative analysis of the chrome ore or of ferro-chromium, the chief difficulty has been in obtaining a convenient method for rendering the chromium soluble. The gravimetric methods of determining the chromium from its solutions were soon abandoned as requiring too much time, and two volumetric methods, viz., the permanganate method of H. Schwartz ("Fresenius Quantitative Anal.," i., §112, 2a), and the bichromate method of Penny ("Fresenius Quantitative Anal.," i., §112, 2b) have since been universally adopted.

The chief problem, viz., the complete decomposition of the ore or of its iron alloy remained for a long time unsolved, and the most widely differing methods have from time to time been proposed for this purpose. It was soon found that a wet decomposition by means of acids in combination with oxidising agents would not produce the desired effect, so that almost all the subsequent methods which were proposed for the decomposition of chrome ores or alloys are based on the oxidising action of mixtures containing in varied proportions and combina-

tions Na_2CO_3 , K_2CO_3 , KNO_3 , KClO_3 , KHSO_4 , KF , $\text{Na}_2\text{B}_4\text{O}_7$, &c., &c.

Some of these methods gave satisfactory results, and have found a very extensive application, as, for instance, the so-called magnesia-method of Dr. J. Clark (14), which was proposed by him as early as 1871.

It may be interesting to mention that six years later Christomanos (20) proposed the above mentioned method as one which had been carefully worked out by himself, for the decomposition of chrome ores. He communicated the very accordant results of about 50 different chrome ores, and thus once more proved the exactness of the magnesia-method, the priority of which undoubtedly belongs to Dr. J. Clark. Another reagent for the decomposition of chrome ores has lately been proposed by J. E. Stead (32). It is the so-called tri-basic reagent, consisting of a mixture of 4 parts lime, 1 part Na_2CO_3 , and 1 part K_2CO_3 , which readily effects a complete decomposition. A very similar mixture, viz., 2 parts Na_2CO_3 + 3 parts $\text{Ca}(\text{OH})_2$, was proposed in 1876 by Dr. R. Kayser (17). In all the methods suggested for the decomposition of chrome ores and alloys special stress was laid upon rendering the time required for complete decomposition as short as possible, and this point, as far as the work-analyst is concerned, is naturally of great importance.

The methods previously mentioned fulfilled this condition in so far that they reduced the time necessary for complete decomposition from about 4 hours to 1 to 2 hours.

With the introduction of sodium peroxide for laboratory use the decomposition of chrome ores and alloys enters into a new phase, and W. Hempel (34) was the first to draw the attention of chemists (in 1893) to the use of this reagent for effecting the decomposition of chrome ores. The experiments which he made were only of a qualitative nature, but during the same year J. Spueller and S. Kalman (35) in Germany and Dr. J. Clark (36) in this country adopted sodium peroxide for the quantitative analysis of chrome ores and alloys, and especially the two first-named chemists succeeded in working out an exact method for the analysis of chrome ore, ferro-chromium, and chrome steel.

The chief claim made for the sodium peroxide was the extraordinary rapidity with which a complete decomposition could be effected, provided that the ore was reduced to a very fine powder.

E. H. Saniter (40) has quite recently also published a

paper upon the subject. In this paper he does not refer to the process of Kalman and Spueller, which we have found to give satisfactory results, and describes his process as "A New Method for the Analysis of Chrome Ore and Ferro-chromium," although it is practically only a modification of Dr. Clark's process. He further states that 3 to 5 minutes are sufficient to decompose even a "moderately finely ground" chrome ore, the very fine grinding thus becoming quite unnecessary. Considering the considerable importance which such an easy and exact way of determination would have for the chromium industry, we thought ourselves justified in undertaking a careful inquiry into the above mentioned methods, and in a recent paper read before the Society of Chemical Industry we have communicated the results at which we have arrived.

We find as a result of this inquiry that sodium peroxide can be used for effecting the fusion of a chrome ore or ferro-chromium if it be reduced to a very fine powder, and that the heating with sodium peroxide must be continued for five minutes in the case of chrome-iron ores, and ten minutes in the case of ferro-chromes. In both cases it is advisable to add a second quantity of sodium peroxide after the melt has partially cooled and then re-heated. After fusion it is essential that the aqueous solution of the melt should be boiled before acidulation for ten minutes in order to effect the complete decomposition of any sodium peroxide which remains still un-reduced.

Before titrating the solution, it is desirable to filter from any oxides of iron or nickel which may be present, since the latter interferes with the end reaction when ferricyanide is used as an indicator. We submit a summary of the papers bearing on this subject which may be of value to those readers of the *CHEMICAL NEWS* who are interested in the analysis of these chromium compounds.

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RAPID DETERMINATION OF NITRIC NITROGEN IN VEGETABLE PRODUCTS.

By P. PICTET.

THE method of determination in question depends on the colouration taken by brucine on contact with nitric acid, free or liberated from a nitrate by the action of concentrated sulphuric acid. A drop of the liquid containing the nitrate is placed upon a plate of porcelain, and there is mixed with it a drop of pure concentrated sulphuric acid. Some fragments of brucine are allowed to fall into the liquid, which is successively diluted with distilled water, the dilution being increased until the colouration ceases to be produced. The method permits of the determination of 1 part of nitric nitrogen in 50,000 parts of water.

Modus operandi.—The organic matter is dried in the stove at 100°, and then finely powdered. We weigh off 2 or 4 grms., according to the supposed proportion of nitric acid. The powder is placed in a small flask with a long narrow neck, and there are added 20 c.c. of distilled water. The flask is rapidly heated to near upon ebullition, so as to avoid the loss of liquid in the state of vapour. At this moment the flask is sealed hermetically, and it is shaken from time to time for a quarter of an hour, leaving the flask in a hot place so as to dissolve the nitrate completely. When cold, we filter the liquid through a layer of animal charcoal, powdered and washed, and resting at the bottom of a funnel on a small plug of asbestos, not too compact. The clear colourless filtrate is received in a small flask which supports the funnel. During filtration the funnel is covered with a slender plate of glass. We thus collect from 10 to 15 c.c. of liquid. The flask is then sealed hermetically until the moment of determination.

For determination we take, with a graduated pipette, exactly 2 c.c. of the liquid, which is transferred to a testing-glass holding 50 to 60 c.c. With a cylindrical glass rod of 3 m.m. in diameter, rounded at its end, we take a drop of the liquid and deposit it upon a plate of white porcelain laid on a horizontal support. With a similar rod, we take from a bottle a drop of pure monohydrated sulphuric acid. We allow this drop to fall carefully upon the nitric liquid and mix the two liquids intimately with a stout platinum wire, spreading them out to the diameter of a 50 centimes coin. Then we throw suddenly into the middle of the liquid, with the point of a penknife, a particle of finely powdered brucine of the

size of a pin's head. An intense red colour at once appears and spreads concentrically. Into the glass we add gradually 2 c.c. of distilled water until the colouration no longer appears. We then make a second more accurate determination, proceeding near the limit by fractions of a c.c. of water.

With a little practice the first determination can be made very rapidly.

Calculation of the Proportion of Nitric Nitrogen.—Let 2 grms. of the dry pulverised substance be digested with 20 c.c. of water. In the assay, in order no longer to obtain a perceptible red tint, we have been obliged to add to 2 c.c. of the solution 10·4 c.c. of water. The volume then becomes $2 + 10·4 = 12·4$ c.c. This liquid contains per c.c. 0·0000207 of nitric nitrogen. But the quantity of this liquid which corresponds to one grm. of solid matter is—

$$12·4 \text{ c.c.} \times \frac{10}{2} = 62 \text{ c.c.}$$

The nitric nitrogen in 1 grm. of the substance is $0·0000207 \times 62 = 0·00128$ grm., or 0·128 per cent.

Determination in presence of a Nitrite.—A nitrite in solution gives the same colouration with brucine and sulphuric acid. Along with the known means for detecting nitrous acid, we may mention pure concentrated hydrochloric acid not containing free chlorine, employed in the same manner as sulphuric acid. It decomposes the nitrites without attacking the nitrates, and enables us to detect with brucine a nitrite in presence of a nitrate.

If we wish to determine nitric nitrogen accurately, we search first for the presence of nitrous nitrogen and determine it by the ordinary methods (Trommsdorf, Griess, Piccini). Then, in testing for brucine with sulphuric acid, when the colouration has diminished in intensity by dilution, we add to the drop of the solution a minute drop of chlorine water, taken with a platinum wire, and mix intimately. After three minutes we add sulphuric acid and then brucine. The action of the chlorine upon the nitrite is very rapid, almost instantaneous, if the nitrite is not very dilute. A slight excess of chlorine does not interfere, and hydrochloric acid is not injurious.

This last experiment shows the totality of the oxidised nitrogen. The presence of a sulphite, a sulphide, or an acetate does not attenuate the colour of the brucine.—*Comptes Rendus*, cxxi., p. 758.

THE TREATMENT OF THE EMERALD AND THE PREPARATION OF PURE GLUCINA.

By P. LEBEAU,

THE procedures used for extracting glucina from the emerald are numerous, but for the most part rather delicate; this mineral being not attackable by acids and containing a large proportion of silica. As the presence of this last substance always complicates the separation of the metallic oxides, we have selected a method which permits of its elimination at the outset in the state of silicon fluoride.

Woehler has often used for attacking silicated minerals the hydrofluoric acid produced in the presence of the pulverised mineral by the action of sulphuric acid upon calcium fluoride. Other acids have replaced the use of the hydrofluorate of a fluoride or of alkaline fluorides.

The Attack of Emerald.

1. On applying Woehler's procedure to the treatment of the emerald, we find that it is difficult to obtain a complete action, especially when using rather considerable quantities of material. This defect may be remedied by melting the emerald at first with calcium fluoride. To this end, we heat from 5 to 6 kilos. of a mixture of 1 part

emerald with 2 parts of calcium fluoride in a large crucible of graphite with a coke fire. When the mass is fluid, it is poured into a trough filled with water, yielding thus a porous material easily pulverised. The attack with sulphuric acid is very brisk, and must be effected in the cold. It is convenient to operate in a large dish of stoneware. When the escape of silicon fluoride has ceased, we heat in the sand-bath until there appear abundant white fumes of sulphuric acid. We then throw it into water by small portions, when aluminium, iron, and glucinum sulphates pass into solution, and there is formed a white deposit of calcium sulphate. The liquid is decanted, the precipitate is washed, and the solutions are concentrated. The excess of acid is then partially saturated with potassium carbonate and the liquid is allowed to cool, when there ensues an abundant deposit of alum, which carries down the chief part of the alumina. The mother-liquors separated from the alum are saturated with ammonia with the further addition of an excess of ammonium carbonate, which is left in contact for some days with frequent stirring. The filtrate on ebullition deposits an impure glucinum and ammonium carbonate, to the purification of which we shall return below.

2. The use of the electric furnace supplies a new and expeditious method for the treatment of the emerald. This mineral if heated in a coke tube readily melts and enters into ebullition. There are disengaged abundant vapours consisting at the outset of almost pure silica, which is deposited as a thick lining at the end of the tube. When, after the experiment, we examine the deposits nearer the heated part we find that their proportion of silica diminishes, though it is still higher than the quantity normally present in the emerald. On the other hand, the more fixed part contains only about half the silica of the emerald, or a mean of 30 per cent. If we operate in a crucible, and stop the heating when the escape of silica—very abundant at first—begins to slacken, there remains a fused substance, always containing a small quantity of lime derived from the furnace, and having the property of becoming pulverised on cooling like potassium bichromate. This silicate, which is more basic than emerald, is directly attackable by acids. We may, e.g., decompose it by hydrofluoric and sulphuric acids, and obtain a solution of sulphates which may be treated as indicated above.

Purification of the Glucina.

The impure glucinum and ammonium carbonate is redissolved in nitric acid, and the dilute solution is mixed with a little potassium ferrocyanide, which throws down all the iron.

We filter, then remove the excess of ferrocyanide by means of copper nitrate; the copper being finally eliminated by means of a current of hydrogen sulphide; we have thus a solution of glucinum nitrate free from iron. It is then only required to separate the alumina which was carried down in the first solution in ammonium carbonate.

To remove these last traces of alumina, we have utilised the property of aluminium hydroxide of being easily polymerised even in the cold, and of thus becoming much less easily attackable by reagents. If we allow the precipitate of hydroxide obtained on treating ammonium nitrate or sulphate with ammonia to remain in the liquid in which it has been formed, it loses its gelatinous aspect and becomes much less easily soluble in acids. It is then completely insoluble in ammonium carbonate.

Glucina free from iron is precipitated from its nitric solution by ammonia. It is left to settle for three or four days, the supernatant liquid is decanted away and is replaced by a concentrated solution of ammonium carbonate, which slowly dissolves the glucina, leaving a slight white deposit of alumina.

The filtrate is heated to ebullition, and the precipitate thus formed is carefully washed and dissolved in pure nitric acid. On evaporating and igniting the solution we

obtain glucina in a dense absolutely pure form. M. Deslandres has kindly examined its spectrum, and has found in it no other metal.—*Comptes Rendus*, cxxi., p. 641.

PROGRAMME OF THE BATAVIAN SOCIETY OF EXPERIMENTAL PHILOSOPHY, OF ROTTERDAM.

AMONG the questions proposed for examination, the following may have a special interest for our readers :—

4. *Question 130.*—An exposition of the anatomical and chemical composition and the vital functions of one, or of more, species of a family of plants represented in Holland or in some of its colonies, and as yet not examined.

6. *Question 141.*—An exact critical review of what is known on the volcanic phenomena of the Indian islands.

9. *Question 154.*—What mode of heating large buildings is the best, most economical, and most sanitary?

10. *Question 155.*—An experimental research into the causes of phosphorescence, especially in the lower animals.

11. *Question 156.*—An experimental research on the electrical properties of some metallic alloys.

14. *Question 164.*—An exact determination of the indices of refraction of similar substances in different parts of the spectrum, and of the absorption spectrum of the same substances.

16. *Question 166.*—An examination of the specific heat of rhombic sulphur above 100°; of monoclinic and amorphous sulphur at different temperatures; of red phosphorus above 100°; and of common phosphorus at different temperatures.

21. *Question 176.*—Monographs on an element, *e.g.*, sulphur; on a class of its combinations; on its compounds with oxygen and carbon; on a phenomenon or series of phenomena, such as the action of sulphuric or nitric acid upon other bodies.

22. *Question 177.*—Very careful experimental determination of the atomic weight of at least one element not as yet sufficiently known.

24. *Question 181.*—A description of the vital conditions and properties of one or more species of moulds, ferments, or bacteria which are important in agriculture, horticulture, in the production of butter, cheese, beer, vinegar, alcohol, &c.

31. *Question 188.*—How long do the bacilli of tuberculosis remain virulent in milk, and especially in butter-milk, under the ordinary conditions of trade?

32. *Question 189.*—How long do pathogenic bacteria originating in the intestinal canal remain virulent in potable waters not sterilised, in flowing waters, in ditch-waters, and well-water?

33. *Question 190.*—A chemical and bacteriological investigation of the water of a river into which flows the sewage water of a great city.

35. *Question 192.*—A research on the origin and physiological signification of the green colouring matter in the bodies of green articulata (animals).

36. *Question 193.*—New researches on the action of sulphur in powder or salts of copper on the disease-parasites of plants.

37. *Question 194.*—A research on the part played by micro-organisms in the transformation of vegetable matter in the soil into humus.

The Society's Gold Medal, of the weight of 30 ducats, will be awarded to the author of the best reply to any of these questions.

The papers must be drawn up in Dutch, French, English, German, or Latin written in Italian characters, in another handwriting than that of the author, and not signed by him, but marked with a motto, and accom-

panied by a sealed envelope bearing the same motto and enclosing the name and address of the author.

The documents must be sent post free to the Chief Secretary, Dr. G. J. W. Bremer, on or before February 1, 1897.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, December 10th, 1895.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 1st to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined three were recorded as "clear but dull," the remainder being clear, bright, and well filtered.

We have this month to record a large excess of rainfall, the quantity measured at Oxford being 4.17 inches, as compared with 2.31 inches (the average for 25 years), showing an excess of 1.86 inches. The rain was chiefly confined to the first half of the month, three-fourths falling during the first fifteen days; there were thirteen days on which no rain fell.

It is satisfactory to be able to report that the Thames-derived waters show a marked improvement in quality when the analyses for the past month are compared with the results for the corresponding period of last year. The Autumnal floods invariably cause a slight increase of colour, and the organic carbon is correspondingly raised.

Our bacteriological examinations give the following numbers of colonies per c.c.

	Colonies per c.c.
Thames water, unfiltered	7400
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	120
Ditto ditto lowest	44
Ditto ditto mean	88
New River water, unfiltered	5000
New River water, from the Company's clear water well	70
River Lea water, unfiltered	2000
River Lea water from the East London Com- pany's clear water well	52

These results show a very high efficiency in the methods of filtration employed by the Water Companies, and that the quality of the supply is excellent.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from vol. lxxii, p. 313.)

Chloride of Potassium from Chloroplatinate of Potassium.

HAVING proved the possibility of purifying chlorate of potassium from all solid impurities, I turned my attention to producing chloride from chloroplatinate of potassium made from chlorate which could be completely volatilised. My object in so doing was to check my previous estimates of the molecular combination of silver with chloride of potassium, and satisfy myself, at the same time, that this chloride was homogeneous.

I prepared the chloroplatinate by the method of fractionating adopted by M. Bunsen for separating potassium, caesium, rubidium, and sodium.

I had procured a very large quantity of chlorate of potassium, freed from foreign metals by the method of successive crystallisations, as I have described on page 668 of my "New Researches on the Laws of Chemical Proportions." The chloride made from it left, on volatilisation, one *five hundred thousandth* part of silica mixed with silicate of potassium and sodium. Moreover it gave, on spectrum analysis, persistent signs of the presence of this last metal.

I have subjected upwards of half a kilogram. of this purified chlorate, in a large platinum distilling apparatus, to three more crystallisations in water made alkaline by 0.1 per cent of hydroxide of potassium made from pure nitre, and containing traces only of sulphide of potassium. I performed the solutions, crystallisations, filtrations, and washings with pure water, in enclosed and purified air as much as possible, taking all the precautions mentioned above, and especially preventing the air from the laboratory passing into the room where I was working, or the air from this room passing into the platinum apparatus.

The chlorate did not show the sodium line after the third treatment, and the chloride which it formed by dissociation was volatilised *without leaving any residue*.

I re-dissolved the chlorate a fourth time, but in pure water, so as to make certain of removing all the hydroxide of potassium used. I thus obtained about *one hundred and fifty grms.* of pure salt, which was at one operation reduced to the state of chloride, by warming it with the greatest care in a large platinum retort with a domed top, and making the arrangements described above, to satisfy myself whether the dissociation was taking place without evolving chlorine. As a matter of fact, I found that the chlorate was transformed into chloride without liberating a trace of chlorine.

The resulting chloride was *neutral* to litmus paper; on spectrum analysis it did not show a trace of the sodium line, and it coloured a Bunsen flame *deep blue*. I have dissolved it in 2 litres of pure water condensed in a *platinum coil*,* and I have poured the solution into a platinum distilling apparatus holding 5 litres, which could be closed with a platinum plug to prevent access of air to it.

Chloride of Platinum.

I have prepared chloride of platinum as pure as it is possible to get it. To do this I dissolved 150 grms. of platinum

* The water used for solutions and washing was condensed in a platinum coil, and kept for use in a very large platinum flask with a platinum stopper. This water was made from spring water distilled in succession:—1st, with a great excess of a very alkaline solution of permanganate of potash, to destroy organic matters; 2nd, with a solution of sulphate of alumina, to eliminate the traces of ammonia always present in water distilled with permanganate; 3rd, alone, to keep back the traces of sulphate of alumina mechanically mixed with its vapour. During the first two distillations the water vapour was condensed in a tin refrigerator. It was only at the third distillation that I used the platinum coil, the upper part of which was turned back and reached far into a socket soldered on to the lid of the distilling chamber, and the lower part was also turned up and passed into the large platinum flask used to store the pure water.

(freed from iridium, rhodium, iron, and silicon in fine flakes, by boiling in hydrochloric acid) in pure aqua regia, held in a Sèvres dish, underneath a glass funnel with its edges turned inwards, thus making a gutter, to which was soldered an open tube meant to carry off the liquid condensed from the fumes given off by aqua regia when attacking the metal, and while evaporating the platinum solution to dryness. The residue was dissolved in pure water. It was dissolved and evaporated three separate times, to eliminate, as much as possible, the nitrous compounds which it obstinately retained.

Whilst the platinum was being dissolved, evaporated, and re-dissolved, the dish and the funnel condenser which held the products were kept in a closed glass case communicating with a ventilating chimney.

The chloride of platinum was brownish red when solid; it dissolved in water, making a clear but reddish yellow solution. Fearing that some platinoso-platinic chloride was present, I raised the solution to boiling-point, and passed a current of washed chlorine through it, by means of a tube through the spout of the funnel, until it was sufficiently concentrated, owing to which it became of an intense orange-yellow colour. Having reached this result I cut off the current of chlorine, and kept the solution at 100° until it ceased to smell of chlorine.

Directly after it was prepared I put the solution into a Bunsen flame, on the end of a fine platinum wire, recently heated to redness; spectrum analysis of the flame showed the sodium line, until the platinum liberated by reducing the chloride was brought to incandescence. A repetition of the experiment in a hydrogen flame gave the same result. *I did not see any other lines.*

The air of the glass case in which I carried on the operations had then brought some sodium to the chloride, because *the materials used in preparing it were quite free from this impurity.*

Whatever might be the source of the sodium, I added pure water to the platinic solution, so as to make a solution with 10 per cent of chloride.

Chloroplatinate of Potassium.

To the platinic solution I added, little by little, stirring it all the time, a sufficient volume of chloride of potassium to change about *four-tenths* of the dissolved potassium compound into chloroplatinate, and I left the precipitate in the filtrate for *twelve hours*, taking care to keep the precipitate in suspension: this was accomplished by removing the platinum plug and stirring the contents.

Modifications of Chloroplatinate of Potassium.—The clear solution was poured off into a large covered platinum vessel. It was a deeper yellow than a cold aqueous solution of chloroplatinate of potassium. I noticed this on several occasions—on precipitating, *when cold*, an excess of a weak solution of potassic chloride by platinic chloride. It suffices to boil the strongly coloured solution; then, by cooling, either quickly or slowly, the liquid loses a great deal of its colour, and at the same time deposits very brilliant, citron-yellow, granular chloroplatinate.

I found the same thing, in a greater degree, when using platinic chloride to precipitate a cold supersaturated solution of chloride of ammonium. The liquid was coloured deep pure yellow; after boiling it, and leaving it to cool, it became quite colourless, depositing orange-yellow crystals of chloroplatinate of ammonium mixed with crystals of sal-ammoniac: this can be easily verified by putting it all into a half-saturated solution of chloride of ammonium, which dissolves the sal-ammoniac without touching the chloroplatinate of ammonium.

There are therefore two varieties of chloroplatinate of potassium and chloroplatinate of ammonium: these are distinguished by their physical state and their relative solubility. These variations are due to the temperature at which these salts of chlorine are formed. If formed *when cold*, they are flocculent, *dull* yellow, and distinctly

soluble in saturated solutions of the alkaline chlorides of which they are partly formed,

If formed at about 100° , these compounds are always granular, crystalline, scarcely soluble when cold in saturated solutions of alkaline chlorides, and are entirely separated, by cooling, from boiling saturated solutions of these chlorides, and especially from chloroplatinate of ammonium.

To return to the precipitated chloroplatinate of potassium left in the platinum apparatus; it was flocculent and of a dull yellow colour. It was distinctly soluble in pure water, colouring it yellow; I put the pasty mass, with the washings from the dish, into a covered platinum retort, and then washed the precipitate by decantation. I continued the washing until the yellow water poured off—when properly concentrated by boiling, cooling, and separating from the crystallised chloroplatinate—*was no longer precipitated by a ten per cent solution of platinic chloride.*

The washing, in the end, had robbed the solution of nearly half the volume of flocculent chloroplatinate made. I noticed, moreover, that during the washing the compound changed slowly from the flocculent to the granular state.

Before proceeding to desiccation, which was done in a covered platinum vessel, sheltered as far as possible from the surrounding air, I took care to put a piece of the chloroplatinate, on a fine platinum wire loop, in a hydrogen flame; it coloured it *greenish blue* from the beginning until the platinic chloride was completely decomposed. The flame then changed to violet-blue. Spectrum analysis of the flame showed, with the potassium spectrum, the sodium line more intense than in a hydrogen flame burning in air at the same time.

On desiccating it at 100° the chloroplatinate was greatly reduced in bulk, and its colour changed to a very brilliant citron-yellow. It was kept in a covered platinum dish, under a bell-jar with *ground and greased* edges, on a smooth sheet of glass, until it was required for reducing in a hydrogen flame.

The washings from the chloroplatinate were added to the filtrate. This liquid, which amounted to about 2½ litres, contained almost *two-thirds* of the chlorate of potassium experimented on.

The liquid, being too much diluted with water to precipitate the amount of chloride of potassium I wished to recover from it, by the addition of 10 per cent of the platinic chloride solution, I concentrated it in the same apparatus, and reduced its volume to about 1350 c.c.

During the concentration a noticeable amount of chloroplatinate of potassium was deposited, and the amount of it increased still more on cooling. I then added to the liquid, little by little, a 10 per cent solution of platinic chloride equal in volume to that used in the first case. I kept the flocculent precipitate suspended in the liquid for a whole day. After this it was left quiet. I then poured off the supernatant liquid, which was strongly tinged with yellow, and proceeded to wash the flocculent chloroplatinate in the platinum retort, exactly as described for the first precipitate. When it was washed the platino-potassic compound resembled the first one in all respects, although it contained the chloro-salt in a granular state. On desiccating it at 100° , in the covered platinum vessel, it became a very brilliant citron-yellow.

When put into a hydrogen flame *before being desiccated*, on a recently heated loop of pure platinum wire, it coloured it first of all *greenish blue*, and then *violet-blue*. Spectrum analysis of the flames showed, side by side with the potassium spectrum, which was identical with that of the first chloroplatinate, the sodium line more distinct than in hydrogen burning in the same atmosphere. Still, the sodium line was no more intense than in the first chloroplatinate.

After desiccation the chloro-salt was kept in a covered platinum dish, under the same bell-jar as the former.

The washings from the chloroplatinate were added to the filtrate; the total amount of liquid was about *two thousand six hundred c.c.* I concentrated it down to *seven hundred c.c.* in the platinum still. On cooling the liquid, a noticeable amount of chloroplatinate was deposited.

Whilst still leaving this compound in the liquid I added to it, *when cold*, little by little, and stirring it continuously, so much of a 10 per cent solution of platinic chloride as would cloud it, so as to eliminate from it all the metal capable of being thus precipitated in the form of chloroplatinate. After leaving it for eighteen hours at rest, I poured off the filtrate, which was very slightly coloured yellow, and washed it by decantation, just as I did with the two former chlorates. The washings had already dissolved more than a third of the volume of chloroplatinate, and, as I could still detect free platinic chloride in them after evaporation, I finished the washing with cold absolute alcohol.

After washing, the chloroplatinate was a citron-yellow, resembling the colour taken by the flocculent chloro-salt when heated to 100° , but without being so brilliant.

When moistened with alcohol and put once more into a hydrogen flame, in a recently heated loop of fine platinum wire, it gave it a greenish blue colour, which soon changed to violet-blue. Spectrum analysis of the flame showed, side by side with the characteristic potassium spectrum, the sodium line just as sharp as in the two former chloroplatinates.

I removed the alcohol from the chloro-salt, and kept it for several days under a bell-jar over sulphuric acid.

The filtrate, containing the excess of platinic chloride used, and the saturated washings from the chloroplatinate, which ought to contain the more soluble chloro-salt if the alkaline chloride used was not chemically homogeneous, were carefully and gradually evaporated in a covered platinum retort, the neck of which reached as far as possible into a flask. When the volume of liquid was reduced by at least three-quarters, and it had already deposited the greater part of the dissolved chloro-salt, I chilled it quickly, so as to make a fine powdery deposit from the chloroplatinate still left in solution.

I got it all from the retort by turning it into a covered platinum funnel, fitted with a fine platinum wire sieve. The new filtrate, containing the bulk of the chloroplatinate, was evaporated to saturation, by boiling in the retort. The chloro-salt, deposited by cooling the concentrated liquid, was added to that already in the platinum funnel, while the new filtrate was put into the platinum retort and evaporated to dryness on the water-bath. The residue, consisting of platinic chloride and chloroplatinate of potassium, was taken up by absolute alcohol, and the whole poured into the platinum funnel containing the chloroplatinate. I then dried the mass of chloro-salt by cold absolute alcohol. Having covered the funnel with a bell-jar, I continued to wash it with alcohol so long as I could detect the presence of platinic chloride in the washings.

Having introduced some chloroplatinate, dried with alcohol, by means of a recently heated loop of fine platinum wire into a hydrogen flame, I found that it coloured this flame greenish blue, changing to a violet-blue. Spectrum analysis of these flames, repeated several times, showed a *potassium spectrum* identical with that of the three preceding chloroplatinates, and the sodium line a little stronger than in these three chloro-salts.

Having found, by the addition of anhydrous ether, that chloroplatinate was present in the alcohol used to wash the chloroplatinate of potassium, I added anhydrous ether until the reaction ceased. To produce this effect, it required a quantity of ether equal to *two-thirds* of the volume of alcohol. The precipitate, when drained by a mixture of equal parts of ether and absolute alcohol, collected, and dried, weighed 0.0474 grm. from 2435 c.c. of etherised alcohol: when very carefully examined I found that the dull yellow precipitate was formed entirely

of chloroplatinate of potassium. In fact, until the alkaline metal it contained was entirely volatilised, it gave the potassium spectrum with the sodium line, in spite of the most careful way the chloroplatinate had been washed with alcohol only.

Wishing to ascertain the nature of the chloro-salt left with the platonic chloride in the etherised alcohol, I added to it, firstly, pure water, and then a solution of pure chloride of ammonium, in sufficient bulk to reduce the platonic chloride to chloroplatinate, and I gradually distilled the whole mass, in the platinum retort, first on a bath, and then on an open fire, so as to completely dry the residue.

I dissolved the residue in boiling water, and evaporated the solution in a *platinum boat*, on a bath, under a damp bell-jar. The chloroplatinate, which was a pale and dull yellow, was reduced in hydrogen at the lowest possible temperature, in the platinum boat in a combustion-tube. I then volatilised the chloride of ammonium produced, in hydrogen. In fact, the chloroplatinate of ammonium was divided in the hydrogen into platinum and chloride of ammonium, below the temperature at which this compound volatilises. The sal-ammoniac formed during the reaction re-forms in a powdery state on the surface of the metal reacted upon.

After the reaction, I put the grey platinum residue in the boat into pure water, and immediately evaporated it in another platinum boat, weighing all the filtered washings in a tube with a ground-glass stopper. The residue after evaporation, previously dried at 150°, was quite white. Its weight, determined by substitution, after cooling it in dry air, was about 0.01375 grm. This residue was highly hygroscopic, and had a *strong alkaline reaction*. I found, on spectroscopic examination, that it consisted entirely of *chloride of calcium, with traces only of sodium and potassium*.

Eighty grms. of chloride of potassium, entirely free from calcium and sodium, were experimented on. I made some platonic chloride from *one hundred and fifty grms.* of platinum prepared by Mr. Matthey, of London, and free from iron, iridium, rhodium, silicon, and sodium. *Eight litres* of pure water, condensed and collected on platinum, were used to dissolve and wash it.

After the numerous experiments I have made on water condensed by means of platinum refrigerators and aqua regia, I am in a position to state that the calcium found in the residue comes from neither the water nor the aqua regia. I must, then, suspect that there is at least a possibility that the calcium has been brought to the platinum, which was melted in a lime crucible, by the air in the glass cage, at the same time as the traces of sodium, in spite of the unremitting care I took to shelter it from atmospheric dust.

Besides, I have found on several occasions that, on remelting welded platinum in an oxyhydrogen blowpipe in the air, and then cooling* it in a lime crucible, the calcium spectrum is visible for several moments.

I reduced separately the chloroplatinate made first and last, and together that made second and third. These reductions were performed in a platinum retort in a magnesia bath, with the same arrangements and in the same manner that I described on pages 675 and 676 of my "New Researches on the Laws of Chemical Proportions," and taking special care to carry it out at the *lowest possible temperature*, so as not to lose the alkaline chloride liberated, and to continue the liberation of hydrogen at this temperature so long as this gas carries hydrochloric

acid with it. I then heated the magnesia bath in which the retort stood, until the mercury, in a tube stopped at one end, when slanted and put deep into the magnesia, began to boil gently. I kept the product of the reduction of chloroplatinate thus for *one hour* in a slow current of pure dry hydrogen, and I thus drove off the hydrochloric acid which was so obstinately held by the alkaline chloride. All the chloroplatinate used was reduced in three operations.

The mass was lixiviated in pure fresh water. The chloride of potassium solution, whether saturated or dilute, was *colourless*, which is never the case when the chloroplatinate is not wholly reduced. This solution, after being filtered through paper which had been washed in succession with dilute hydrofluoric and hydrochloric acids and with pure water, and being evaporated in platinum under a bell-jar, left a white saline residue, which, when melted in a covered platinum crucible, formed a liquid free from any trace of platinum in suspension. *This liquid, when poured into a platinum vessel, formed a clear and colourless button.*

A part of the three melted chlorides, when dissolved in water, made a perfectly clear solution, *neutral* to litmus paper and also to phenolphthalein. This solution coloured a hydrogen flame *violet-blue*. Spectrum analysis of the flame showed the sodium line in *all three chlorides*, as well as the potassium spectrum, and clearer than in the same hydrogen burning in air. As a check, I put into the flame some chloride made from the chlorate, used in preparing the chloroplatinate, and a comparison showed the same result.

I proved that the spectra of all *three chlorides* obtained from chloro-platonic salts were *identical*, and, *excepting for traces of the sodium line, that they were identical with the spectrum of the chloride used in preparing the chloroplatinates.*

The long and delicate work in which I was engaged, by using *large and costly platinum apparatus, which were generously lent to me*, thus confirmed the results of my previous researches on the homogeneity of potassic chloride made from chloroplatinate, and showed once more that I was not able to procure by this means a chloride which did not show the sodium line.

By the method described in a previous note I evaporated, successively, on a flat dish of pure platinum, *five grms.* of chloride made during the *first and last* reductions, and *ten grms.* of chloride from the chloroplatinates made during the *second and third* precipitations. These three masses of chloride were volatilised without leaving on the platinum dish a trace of residue visible under a microscope.

Excepting for minute traces of sodium brought by the platonic chloride, those three parts form the body which combines with platonic chloride, and their molecular affinity to silver ought to be the true affinity of this metal for chloride of potassium, regarded as a distinct substance, if, as is probable, if not certain, *owing to the identity of their spectra*, future experiments show that they are identical among themselves and with the chlorides from chlorate and perchlorate of potassium.

In a special article I shall describe the researches I undertook in order to throw light on these different questions.

(To be continued).

Messrs. F. Wiggins and Sons, Mica Merchants, wish to notify that, owing to the great increase of business necessitating additional warehouse room, they have purchased No. 103, Minories, and that during the demolition and re-building of that and their old house, No. 102, Minories, they have taken temporary premises at Nos. 62 and 63, Minories (opposite), where for the next twelve months all communications should be addressed, or to their other establishment, 10, Tower Hill, London.

* Since the conclusion of these researches and the publication of this note, Mr. Matthey, of London, has sent me for examination a specimen of *very bright spongy platinum*, made by *volatilisation* during the process of completely fusing this metal on a large scale, in oxy-coal gas, in a lime crucible. This sponge, on exposure to damp air, is quickly dulled, by coating itself with hydrocarbonate of calcium. On separating the calcic hydrocarbonate by means of dilute hydrochloric acid, the residual platinum is quite dull and of a bluish grey tint. It is probable that the bright sponge, whiter than platinum, consists of an alloy of calcium and platinum.

THE PREPARATION OF PERCHLORIC ACID AND ITS APPLICATION TO THE DETERMINATION OF POTASSIUM.*

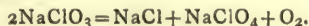
By D. ALBERT KREIDER.

VARIOUS methods for the preparation of perchloric acid have been developed through the long felt want of a process in which the elements of time and danger would be reduced to a minimum and the product increased to quantities commensurate with the growing use of the acid in analytical chemistry. Most of these methods have been found impracticable because of the incidental formation of the dangerously explosive oxides of chlorine, or the time required in refining the product from the impurities introduced with the reagents employed.

Doubtless the best process thus far offered is that of Caspari (*Zeitschr. für Ang. Chem.*, 1893, p. 68), which, however, is to an objectionable degree exacting of time and labour. The product has to be treated and re-treated for the removal of potassium and then for the extraction of the hydro-fluosilicic acid, and at several stages is for this purpose to be left standing for from 24 to 48 hours. Under the most favourable circumstances it could not be prepared in less than 5 or 6 days, and during a great many hours of that time it requires close attention.

The great difficulty has always been with the necessity of a perfect separation of potassium from the perchloric acid, which has been prepared by the ignition of the potassium chlorate. If, for the manufacture of the perchlorate, the chlorate of sodium—which, if not upon the shelves of every laboratory, is nevertheless in the market, almost, if not entirely free of potassium—be used instead of the potassium salt, the complete removal of the base will be unnecessary; since its presence in the determination of potassium will exert no influence other than that which is beneficial. It is well known that because of its deliquescence and the almost equal solubility of sodium perchlorate with that of the chloride, its separation from the latter by re-crystallisation from an aqueous solution, as in the case of potassium, is impossible. But the insolubility of the chloride of sodium in strong hydrochloric acid, with the aid of the acid-proof Gooch crucible, affords a means for the liberation of the perchloric acid and the removal of the greater part of the sodium in one operation. Upon this basis, therefore, the following simple method was elaborated.

A convenient quantity of sodium chlorate, from 100 to 300 grms., is melted in a glass retort or round-bottomed flask and gradually raised to a temperature at which oxygen is freely, but not too rapidly, evolved, and kept at this temperature till the fused mass thickens throughout, which indicates the complete conversion of the chlorate to the chloride and perchlorate, and requires between one and one-half to two hours; or the retort may be connected with a gasometer and the end of the reaction determined by the volume of oxygen expelled, according to the equation—



The product thus obtained is washed from the retort to a capacious evaporating dish, where it is treated with sufficient hydrochloric acid to effect the complete reduction of the residual chlorate, which, if the ignition has been carefully conducted with well distributed heat, will be present in but small amount. It is then evaporated to dryness on the steam bath, or more quickly over a direct flame, and with but little attention until a point near to dryness has been reached, when stirring will be found of great advantage in facilitating the volatilisation of the remaining liquid and in breaking up the mass of salt. Otherwise the perchlorate seems to solidify with a certain amount of water, and removal from the dish, without moistening and re-heating, is impossible.

After trituration the residue, easily accomplished in a porcelain mortar, an excess of the strongest hydrochloric acid is added to the dry salt, preferably in a tall beaker, where there is less surface for the escape of hydrochloric acid, and from which the acid can be decanted without disturbing the precipitated chloride. If the salt has been reduced to a very fine powder, by stirring energetically for a minute, the hydrochloric acid will set free the perchloric acid and precipitate the sodium as chloride, which in a few minutes settles, leaving a clear solution of the perchloric acid with the excess of hydrochloric acid. The clear supernatant liquid is then decanted upon a Gooch filter, through which it may be rapidly drawn with the aid of suction, and the residue re-treated with the strongest hydrochloric acid, settled and again decanted, the salt being finally brought upon the filter, where it is washed with a little strong hydrochloric acid. A large platinum cone will be found more convenient than the crucible, because of its greater capacity and filtering surface. When the filter will not hold all the sodium chloride, the latter after being washed may be removed by water or by mechanical means, with precautions not to disturb the felt, which is then ready for the remainder. Of course, if water is used, the felt had better be washed with a little strong hydrochloric acid before receiving another portion of the salt. This residue will be found to contain only an inconsiderable amount of perchlorate, when tested by first heating to expel the free acid and then treating the dry and powdered residue with 97 per cent. alcohol, which dissolves the perchlorate of sodium, but has little soluble effect on the chloride.

The filtrate containing the perchloric acid with the excess of hydrochloric acid and the small per cent of sodium chloride which is soluble in the latter, is then evaporated over the steam bath till all hydrochloric acid is expelled and the heavy white fumes of perchloric acid appear, when it is ready for use in potassium determinations. Evidently the acid will not be chemically pure because the sodium chloride is not absolutely insoluble in hydrochloric acid; but a portion tested with silver nitrate will prove that the sodium, together with any other bases which may have gone through the filter, has been completely converted into perchlorate, and unless the original chlorate contained some potassium or on evaporation the acid was exposed to the fumes of ammonia, the residue of the evaporation of a portion is easily and completely soluble in 97 per cent alcohol, and its presence is therefore unobjectionable. One c.c. of the acid thus obtained gave on evaporation a residue of only 0.036 gm., which was completely soluble in 97 per cent alcohol.

Caspari's acid under similar treatment gave a residue in one case of 0.024 gm. and in another 0.047 gm. If, however, a portion of pure acid be required, it may be obtained by distilling this product under diminished pressure, and, as Caspari has shown, without great loss providing the heat is regulated according to the fumes in the distilling flask.

Some modification of the above treatment will be found necessary in case the sodium chlorate contains any potassium as an impurity, or if the latter has been introduced from the vessel in which the fusion was made. Under these circumstances the hydrochloric acid would not suffice for the removal of potassium, since a trace might also go over with the sodium, and thus on evaporation a residue insoluble in 97 per cent alcohol be obtained. To avoid this difficulty, the mixture of sodium perchlorate and chloride, after being treated with hydrochloric acid for the reduction of the residual chlorate, being reduced to a fine powder, was well digested with 97 per cent alcohol, which dissolves the sodium perchlorate but leaves the chloride as well as any potassium salt insoluble. By giving the alcohol time to become saturated, which was facilitated by stirring, it was found on filtering and evaporating that an average of about 0.2 gm. of sodium perchlorate was obtained for every c.c. of alcohol, and that

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xlix., June, 1895.

the product thus obtained was comparatively free of chlorides, until the perchlorate was nearly all removed, when more of the chloride seems to dissolve. This treatment with alcohol is continued until, on evaporation of a small portion of the latest filtrate, only a small residue is found. The alcoholic solution of the perchlorate is then distilled from a large flask until the perchlorate begins to crystallise, when the heat is removed and the contents quickly emptied into an evaporating dish, the same liquid being used to wash out the remaining portions of the salt. When the distillation is terminated at the point indicated, the distillate will contain most of the alcohol employed, but in a somewhat stronger solution, so that it requires only diluting to 97 per cent to fit it for use in future preparations. The salt is then evaporated to dryness on the steam bath and subsequently treated with strong hydrochloric acid for the separation of the perchloric acid.

One c.c. of the acid prepared in this way on evaporation gave a residue in one case of 0.0369 grm., and in another 0.0307 grm., completely soluble in 97 per cent alcohol, which was then ignited and the chlorine determined by silver, from which the equivalent of perchloric acid in the form of salts was calculated as 0.0305 grm. By neutralising the acid with sodium carbonate, evaporating, igniting in an atmosphere of carbon dioxide till decomposition was complete, collecting the oxygen over caustic potash, allowing it to act on hydriodic acid by intervention of nitric oxide, according to a process soon to be published, titrating the iodine liberated, with standard arsenic and calculating the equivalent of perchloric acid, after subtracting the amount of acid found in the form of salts, the amount of free acid per c.c. proved to be 0.9831 grm.

The whole process, even when the separation with alcohol is necessary, can not well require more than two days, and during the greater part of that time the work proceeds without attention.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 5th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from vol. lxxii., p. 316).

148. "Derivatives of α -Hydrindone." By C. REVIS and F. STANLEY KIPPING, Ph.D., D.Sc.

The study of α -hydrindone (*Trans.*, 1894, 480) has been continued, and attempts have been made to convert it into $\alpha\beta$ -diketohydrindone; up to the present, however, this substance has not been obtained.

Two compounds are formed on treating α -hydrindone with a solution of bromine in soda according to the conditions of the experiment; if the ketone be simply shaken with the alkaline solution at ordinary temperatures, it is slowly converted into a bulky mass consisting of ordinary dibromohydrindone (m.p. 132°), whereas if the mixture be heated on the water-bath a heavy crystalline powder is formed, apparently by further action on the dibrom-compound. The latter is very sparingly soluble in most ordinary solvents, but may be crystallised from boiling acetic acid, from which it separates in long colourless needles decomposing between 250° and 260°. Analyses show it to be a condensation product of the composition $C_{18}H_{12}O_3$, but its constitution has not yet been established.

When monobromohydrindone is dissolved in alcoholic potash at ordinary temperatures it furnishes a substance which crystallises from chloroform in large, transparent,

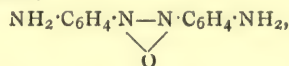
well-defined prisms. This compound is a condensation product of the composition $C_{18}H_{13}BrO_2$.

Dibromohydrindone (m.p. 132°) is readily acted on by alcoholic potash yielding various products according to the conditions of the experiment.

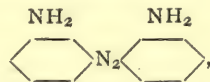
If the potash be added gradually until the solution becomes permanently alkaline, the dibromo-derivative is converted into a new substance, which crystallises from benzene in lustrous needles of indefinite melting-point (decomposing from 150° to 160°).

149. "The Alkaline Reduction of Metanitrilaniline." By RAPHAEL MELDOLA and ERNEST R. ANDREWS.

On heating an aqueous solution of metanitrilaniline with alkaline reducing agents, such as sodium stannite, the azoxy-compound,—



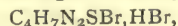
scales (from toluene) or needles (from boiling water or dilute alcohol); m.p. 146—148°. The diacetyl-derivative (m.p. 254°), the disazimide (m.p. 86—85°), the disazo- β -naphthol derivative (m.p. 244—245°), and the metadiiodo-azoxybenzene (m.p. 118—119°), have been prepared from the diamidoazoxy-compound. The corresponding azo-compound, having the constitution—



has been prepared by the complete reduction of the azoxy-compound to a hydrazo-compound by the action of zinc-dust and alkali, and subsequent re-oxidation. This has been found the most effective way of obtaining the azo-compound in a state of purity. It consists of dull orange needles when crystallised from boiling water; m.p. 150—151°. The diacetyl-derivative (m.p. 272°), the dibenzoyl-derivative (m.p. 284—285°), the disazo- β -naphthol (m.p. 282°), and the oxalate of the base have prepared, and are described in the paper. The constitution was confirmed by conversion into the metadiiodoazobenzene (m.p. 150—151°) of Gabriel (*Ber.*, 1876, ix., 1410). Both the azoxy- and azo-compounds are well-characterised bases forming diacid salts. The paper concludes with a theoretical discussion by one of the authors (Meldola) of the process of reduction of nitro-compounds.

150. "The Chemistry of Dibromopropylthiocarbimide; and the Action of Bromine and Iodine upon Allylthiourea." By AUGUSTUS E. DIXON, M.D.

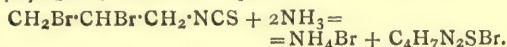
Having failed to obtain dibromopropylthiourea from $\beta\gamma$ -dibromopropylthiocarbimide and ammonia (*Trans.*, 1892, lxi., 548), the author proceeded to re-examine a compound obtained by Maly (*Zeits. f. Chem.*, 1867, 42) from allylthiourea and bromine. This compound, "thiosinnamine dibromide," $C_4H_8N_2SBr_2$, is, however, not dibromopropylthiourea, but proves to be the hydrobromide of a well-marked base, $C_4H_7N_2SBr$, which is precipitated, on the addition of caustic alkali, as a dense, almost colourless, strongly alkaline oil. The oil is sparingly soluble in water; it combines with hydrochloric acid to form the hydrochloride, $C_4H_7N_2SBr \cdot HCl$, hard white prisms melting at 129—130°, and identical with the "bromochloride" obtained by Maly from "thiosinnamine dibromide" and moist $AgCl$. The hydrobromide,—



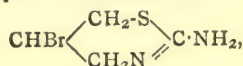
from the base and HBr , is identical with the dibromide; it was found to melt at 139—140°. By treatment of either the free base or its hydrobromide with picric acid, the salt $C_4H_7N_2SBr \cdot C_6H_2(NO_2)_3OH$ is precipitated; when re-crystallised from dilute spirit it forms minute, glittering prisms, pale yellow in colour, and melting at 187—188°.

Heat is evolved on mixing dibromopropylthiocarbimide

with alcoholic ammonia; ammonium bromide separates, and is left, together with a brownish syrup, when the alcohol is evaporated: this syrup is the brominated base $C_4H_7N_2SBr$, somewhat impure.

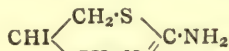


Reasoning from the conditions under which the base is produced, from its alkaline character, and from the fact that it is not desulphurised by treatment with alkaline lead, or ammoniacal silver solutions, the author regards it as having the probable constitution—



i.e., μ -amido- γ -brompenthiazoline, otherwise β bromotrimethylene- ψ -m-thiourea. This view also receives support from the results of experiments by Gabriel and others, on the interaction of brominated fatty bases with thiocarbimides, whereby the tendency has been shown of monohalogenised fatty thioureas to lose, at the moment of formation, their contained halogen, with production of the corresponding haloid salts of closed-chain bases of the above type.

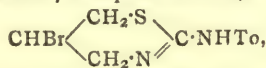
Iodine appears not to combine with allylthiocarbamide, but acts similarly to bromine on allylthiourea, giving the hydriodide of an iodised base, $C_4H_7N_2SI \cdot HI$. The salt is freely soluble in water or spirit, and melts at $132.5-133.5^\circ$. When treated with caustic potash the base is thrown down as a dense, sticky oil, alkaline to litmus, nearly insoluble in water, reacting (like its brominated analogue) for halogen with chlorine water, and yielding a picrate of m. p. $176-177^\circ$. The constitution assigned to it is—



= μ -amido- γ -iodpenthiazoline.

Similar compounds were obtained by acting with organic bases upon dibromopropylthiocarbimide.

μ -Orthotolylamido- γ -brompenthiazoline,—

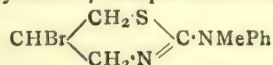


from the thiocarbimide and o-toluidine, was deposited from alcohol in rhombic plates, m. p. $134.5-135.5^\circ$. It is insoluble in water, rather difficultly soluble in alcohol, feebly alkaline to litmus, and—like the other compounds of its class—retains its sulphur, even when boiled with alkaline lead, or ammoniacal silver salts. The hydrobromide is a clear, pale brown, apparently uncrystallisable, acid syrup.

μ -Paratolylamido- γ -brompenthiazoline hydrobromide, formed a thick, acid syrup; the free base occurred in rosettes of pointed white prisms melting at $124-125^\circ$.

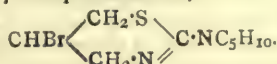
μ -Naphthylamido- γ -brompenthiazoline, like its hydrobromide, could only be obtained as a liquid. The hydrobromide of the corresponding β -naphthyl compound was a brownish, tenacious acid syrup; its base occurred in brilliant prisms, neutral at litmus, and melting at $190-191^\circ$.

μ -Methylphenylamido- γ -brompenthiazoline,—



(from the thiocarbimide and methylaniline, with evolution of heat), separated as a colourless oil; its hydrobromide is crystalline, easily soluble in hot water, and melts at $183-184^\circ$.

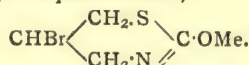
μ -Piperidyl- γ -brompenthiazoline,—



Produced with evolution of heat; the HBr salt forms colourless, vitreous prisms, soluble in cold water, with neutral reaction; m. p., $189-190^\circ$. The base is a nearly colourless syrup, which does not afford bromine when mixed with chlorine water: it is so strongly alkaline as to allow of titration by standard acid.

By acting with methylic, ethylic, and propylic alcohols respectively at a little over 100° on the thiocarbimide, the three following compounds were obtained, together with (free) hydrogen bromide.

μ -Methoxy- γ -brompenthiazoline,—

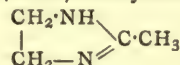


White crystals easily soluble in hot water; not desulphurised by silver or lead salts; m. p., $95-96^\circ$. The silver compound becomes purple on short exposure to actinic light.

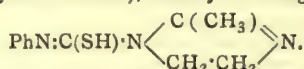
μ -Ethoxy- γ -brompenthiazoline.—Small white prisms, moderately soluble in hot water; m. p., $96-97^\circ$. Forms a silver compound which is very markedly light-sensitive.

μ -Propoxy- γ -brompenthiazoline.—Pyramidal crystals; m. p., $96-97^\circ$; closely resembling the preceding compound in properties.

Phenyl and orthotolylthiocarbimides respectively combine, evolving heat, with μ -methylimidazoline,—



(ethenylethylene diamine), thereby affording—



μ -Methylimidazolylphenylthiourea.—Thick, lustrous prisms, difficultly soluble in cold water or alcohol; desulphurised by lead and silver salts; m. p., $173-174^\circ$.

μ -Methylimidazolyl-o-tolylthiourea.—White crystals, melting at $159-159.5^\circ$, and generally resembling the corresponding phenyl-derivatives.

Helmholtz Memorial Lecture.

The Helmholtz Memorial Lecture will be delivered by Professor G. F. Fitzgerald, F.R.S., at an extra meeting of the Society to be held on Thursday, January 23, 1896, at 8 p.m.

NOTICES OF BOOKS.

Service Chemistry: being a Short Manual of Chemistry and its Applications in the Military and Naval Services. By VIVIAN B. LEWES, F.I.C., F.C.S., Professor of Chemistry, Royal Naval College, Greenwich; Associate of the Institution of Naval Architects, &c. Second and Revised Edition, Illustrated. 8vo., pp. 558. London: W. B. Whittingham and Co., Limited, Gracechurch Street, E.C.

THE author of this text-book does not fail to remind his readers that there is but substantially one chemistry, alike for the military and naval officer, for the metallurgist, the medical man, the agriculturist, or the dyer, and that its special adaptation to any one subject is merely an expansion of this one Science in some given direction. Few of the applications of our Science, indeed, are so manifold as those involved in the military and naval arts. They include the doctrine of explosives, the properties of metals and their alloys, as manifested in ordnance, in the sheathing and armour coating of ships, and sanitary chemistry in the most varied sense of the term. It is perhaps fortunate that no one class of experts is

responsible for all these departments. Thus the medical officer—if in these days he is duly listened to—is, or should be, alone entitled to decide on the fitness of a drinking water supply, whether on ship-board or for troops on the march. At the same time the tendency of any water to form "crock," or to corrode boiler plates, is on the home-stations committed to a technical chemist, and during long voyages may fall into the hands of the chief engineer.

After a clear, but necessarily brief, exposition of the fundamental principles of chemistry, we find an account of electrolysis, with especial reference to the mutual relations between different metals on ships' bottoms, and to the arguments for and against the use of zinc protectors. Three important chapters are given to the properties and purification of waters. The filtering material which is found most satisfactory is "cabalite," the composition of which is not stated.

There is no mention of Pasteur's (Chamberland's) filter, which, though probably the most efficient known, is too slow in its action for supplying a ship's company, and would be too cumbersome for troops on the march. The peril of drinking unfiltered water in tropical countries is great, since it may contain the germs of the *Filaria*. Even in temperate and cold climates it may serve as a medium for the introduction of hydatidous disease, which is always a possible contingency in any water to which dogs have access, alike in chilly Iceland and in hot Queensland. It is not generally known that in times of drought, in the latter country, the shepherds and stockmen will drink from a water-hole in which a sheep or a bullock is putrefying, whilst they utterly avoid one containing the remains of a dog.

It is to be hoped that due provision has been made for ensuring a safe water-supply for our troops on the Ashanti expedition. In the last Ashanti war the addition to the water of a mixture of alum, clay, and charcoal, as recommended by Mr. Crookes, was found very serviceable.

As a matter of course explosives receive prominent attention in the work before us. The number of such compounds and mixtures is now excessive, though but few of them are likely to be of practical importance. Melinite—the much-extolled French explosive—has been, the author considers, over-rated. If it was used in the late Madagascar war, no phenomena are recorded which could be traced to its action. Its main ingredient is picric acid. This acid has been repeatedly patented in different mixtures, and it has been officially experimented with both in Britain and Germany. The "smokeless powder" adopted in the British services—cordite—is a mixture of 58 per cent nitroglycerin, 37 per cent trinitrocellulose, and 5 per cent of vaselin. It is made at the Government works at Waltham Abbey, and evidently requires great care and skill in its manufacture and storage, as several accidents have occurred at the works. It is found, as the author tells us, to withstand the cold of a Canadian winter, or the heat of an Indian summer, without accident or detriment. He recommends that on board ship it should be kept in water-jacketed magazines. No complaints of inconvenience from its combustion-products have been raised either from the army or the navy.

Accidents from "fire-damp" might seem to be outside the scope of Service Chemistry. But, unfortunately, explosive gaseous mixtures may be generated in the coal-bunks of a large steamer, and the same precautions are required as in a coal-mine. Safety lamps are requisite if the coal requires to be moved.

The storage of coal in a wet or broken state may lead to spontaneous combustion. A careful inquiry has been made by Government as to the kinds of coal required for service purposes, and the conclusion comes to is that a mixture of two-thirds Welsh and one-third North-country coal is recommended for use in the Navy.

This work will commend itself to the use of the authorities in both Services.

Direct Spectral Analysis of Minerals. (Analyse Spectrale Directe des Minéraux). By M. ARNAUD DE GRAMONT, Doctor in Science. 8vo., pp. 207. Paris and Liege: Baudry and Co. 1895.

In this little work M. de Gramont suggests and explains a novel method for the spectroscopic examination of minerals. He has observed that many minerals possessing a metallic lustre, such as galena and pyrites, are such good conductors that an electric spark may easily be caused to pass over between their fragments. He has therefore undertaken to study if the spectroscopic examination of such sparks may not furnish a new method for a direct qualitative examination of the elements present in the minerals in question.

After describing the appliances necessary—far from complicated—the author remarks that minerals which are electro-conductive, or even which are only volatilised in the spark, behave spectroscopically like alloys, though like alloys in which the non-metals also give line-spectra like the metals. It is only needful to take into consideration certain rays of the air which persist among those of the elements of the mineral, and which are found laid down in a table.

M. de Gramont's researches lead him to the opinion that this method of examination will be serviceable in mineralogy, metallurgy, and in qualitative analysis, and will often indicate the presence of substances occurring in quantities so small as not to be detected by the wet way.

The work before us gives a description of the apparatus for producing the spark, and then that of the dispersive apparatus used in its spectral analysis.

It then gives an account of the behaviour of each of the elements under the conditions experimentally ascertained.

The tables of the wave-lengths of the minerals studied are very elaborate, and will prove extremely useful in research.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 24, December 9, 1895.

M. Marey's Official Visit to the Royal Society.—M. Marey, in his character as President of the Academy of Sciences, was present at the Anniversary Meetings of the Royal Society. In giving an account of his mission he refers to the expressions of esteem and friendship for the *savants* of France which were uttered by the retiring President, Lord Kelvin, and by his successor designate, Sir J. Lister. The main subject of the meetings was the proposed creation of a grand international catalogue of all the works published in the entire world on all branches of Science. It is well known that the Royal Society has already published a catalogue showing under the name of each author a list of all his writings from the year 1800 downwards. But such a catalogue fails to indicate the researches published on any given subject. To fill up this deficiency the Royal Society proposes to address all Governments through diplomatic channels, to appoint delegates to an international conference to agree on the best means of carrying out this project.

Analysis of Aluminium and its Alloys.—Henri Moissan.—This paper will be inserted in full.

Appreciation of Flours for Baking Purposes. Determination of Remnants of Bran and Germ which may Diminish the Yield of Bread.—Aimé Girard.—This paper also will appear at some length.

Analysis of Soils by Plants.—G. Lechartier.—This paper also will be inserted in full.

Absorption of Nitrogen by Cold Lithium.—H. Deslandres. — M. Gantz has announced recently (*Comptes Rendus*, 1895, p. 777) that lithium prepared by his method absorbs nitrogen rapidly and even with incandescence at temperatures below dull redness. I am indebted to the courtesy of M. Berthelot for some fragments of this lithium, and I have repeated this experiment with atmospheric nitrogen for the preparation of argon, and with the gas from the springs of Maizières (Côte d'Or) to effect its spectroscopic analysis, at the request of M. Moureu. But I observed at the same time a notable escape of hydrogen; therefore to eliminate this gas I was obliged first to heat the lithium in a vacuum for some hours at a temperature below the softening point of ordinary glass. The lithium scarcely melts, and its surface, which is covered with a dull blackish layer, splits up and shows at many points the brilliant metal. At the same time a metallic specular deposit is formed on the cold sides of the glass. If we then introduce the nitrogen, the tube being well cooled and no heat being applied, we observe a slow absorption of the gas in the cold analogous to the slow absorption of oxygen by phosphorus in the cold. The absorption is complete, for the spectral bands characteristic of nitrogen disappear absolutely. The dull blackish layer above mentioned is formed on contact with the air. If we cut a piece of lithium the freshly cut surfaces are brilliant like those of sodium, but tarnish rapidly. Now this dull blackish layer appears to be an obstacle to the action of nitrogen and lithium. As long as it is continuous, without fissures, no absorption takes place. On the contrary, the absorption is the more rapid the larger the surface of the lithium laid bare at the commencement of the experiment. I thought it useful to mention this property of lithium since we do not yet know any substance which absorbs nitrogen alone in the cold.

Possible Process for the Separation of Argon and Atmospheric Nitrogen.—Claudius Linb.—Will be inserted in full.

Action of Alcohol upon Mercurous Iodide.—Maurice François.—Boiling alcohol decomposes mercurous iodide. The decomposition ceases when 100 grs. of the liquid contain in round numbers 0.220 grm. of mercuric iodide in solution. This reaction is reversible, and the inverse action stops at the same limit. The quantitative separation of mercuric and mercurous iodides by means of alcohol is not exact.

New Synthesis of Pararosaniline and its Mono-, Di-, Tri-, and Tetra-Alkylated Derivatives.—Maurice Prud'homme.—The limited reduction of nitrobenzene gives rise to phenylhydroxylamine, which mineral acids convert into para-amidophenol (the reciprocal transformation of the hydroxyl of the radicle NH.OH and of the hydrogen in the para-position next to this radicle. The shade of the series of rosanilines becomes gradually more violet as the number of alcoholic radicles in the amidogenic groups is increased.

Mode of Decomposition of some Organic Bodies of Amidic and Imidic Functions.—Oechsner de Coninck.—The author has extended the method of Leconte and Yvon to the amides and imides of the fatty and of the aromatic series.

Limits of Approximation given by the "Grisometer" with a Platinum or Palladium Wire for the Determination of Formene Gas.—J. Coquillion.—This paper is not suited for useful abstraction.

Distribution of Boric Acid in Nature.—H. Jay.—Boric acid is distributed over the chief part if not over the entire globe. Plants, whether cultivated or wild, absorb from the soil and the water any boric acid which they meet with. Boric acid if introduced in small doses into the stomach of animals, is not assimilated, but is eliminated in the urine and other excretions.

Solubility and Activity of Soluble Ferments in Alcoholic Liquids.—A. Dastre.—The proteolytic ferment trypsin is soluble in alcoholic liquids of percentages up to 55°. The solubility is well marked at from 10 to 25 per cent, and then diminishes rapidly up to 50 per cent. The amylolytic ferment is still more soluble. Its solubility follows an analogous course to that of the foregoing, but extends up to 65 per cent. The ferments of the blood are sparingly soluble in alcoholic liquids, and cannot be recognised with solutions at 4 or 5 per cent.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Society of Chemical Industry, 8. "A Technological Study of Comparative Affinities in the case of certain Salts of Ammonia," by Watson Smith, F.C.S. "Colour Effect of Lime Salts on Hops in Brewing," by J. W. Lovibond.

TUESDAY, 7th.—Royal Institution, 3. (The Christmas Lectures). "Sound, Hearing, and Speech," by Prof. J. G. McKendrick, M.D., F.R.S.

WEDNESDAY, 8th.—Society of Public Analysts, 5. (Annual Meeting). "Determination of Oxygen in Commercial Copper," by Bertram Blount. "Note on a Series of Analyses of a Private Water Supply," by E. Russell Budden. "Note on the presence of Petroleum Oil in a Sample of Whisky," by W. F. Lowe.

THURSDAY, 9th.—Royal Institution, 3. "Sound, Hearing, and Speech," by Prof. J. G. McKendrick, F.R.S.

FRIDAY, 10th.—Astronomical, 8.

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B.Sc. (Vict.), Ph.D. (Heid.), Sc.D. (Dubl.), LL.D. (Glasg.), F.R.S. Principal of the Government Laboratories, London; a Fellow of the University of London; sometime Professor of Chemistry in the Royal College of Science, South Kensington, London; and one of the Examiners in Chemistry of the University of London, and of the Department of Science and Art.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1885.

ON THE SOLUBILITY OF SILICA.

By Prof. ARTHUR M. EDWARDS, M.D., Newark, N.J.

I HAVE been considerably puzzled to find out just what was known respecting the solubility of silica, especially as it comes into my work just now. I am engaged in examining the soundings brought home by the U.S.S. *Tuscarora* made during the seasons of 1873 and 1874. They were placed in my hands by the Academy of Natural Sciences of California to report, where, at San Francisco, Cal., they were left by Commander George E. Belknap. The steamer crossed the Pacific Ocean several times, from the United States to Japan, and made soundings, one of which was in 4655 fathoms, the deepest that has been gotten. They were often in the "red clay" era of Professor Wyville Thomson, and sometimes in the "diatom ooze" of the same gentleman, taken during the celebrated voyage of H.M.S. *Challenger*. In fact, they crossed the line of the *Challenger*, and some of them are the same soundings as brought home by Captain Nares. What I got upon the solubility of silica were the following. Roscoe and Schorlemmer, in their "Treatise on Chemistry," vol. i., p. 566, say that there is only one oxide of silicon, the silicon dioxide or silica, SiO_2 . "It is found not only in the mineral, but in the vegetable and animal kingdoms, existing in large quantities in the glassy straw of the cereals and of bamboos, in the scales of the diatomaceæ, and in the feathers of certain birds, which have been found to contain as much as 40 per cent of this substance. The minute and beautifully formed spicules of the spongiæ and radiolarie also consist of pure silica."

"These are the organisms, the diatomaceæ (now known as the bacillariaceæ), the spongiæ, and the radiolarie, which I have to deal with, and I think there is not enough known of the chemistry of their shells. I will endeavour to make plain what I have discovered after over 40 years studying them. Silica, or quartz, occurs in three states. As quartz it crystallises in combinations of the hexagonal prism with the rhombohedron, with a specific gravity of 2.6 and a hardness of 7. It is colourless or slightly coloured by iron, manganese, or organic matter commonly."

The second form is tridymite. It crystallises like quartz in the hexagonal system, and is found in the trachytic porphyry at Pachuca, in Mexico. It has a specific gravity of 2.3, and hardness of 7.

The third form is amorphous silica, and occurs in nature not as a crystalline mass, but as opal. It is colourless, or variously coloured; specific gravity of 2.3. And not unfrequently crystals of tridymite are found in the non-transparent portions of opal. Chalcedony, agate, and flint are the common varieties. It has a specific gravity of 2.2 when melted, as it can be by the oxy-hydrogen flame.

"In all three conditions silica is insoluble in water, and also in all acids except hydrofluoric, in which it readily dissolves. Silica, however, is easily soluble in all alkalis, even in ammonia, and the more easily the finer its state of division. The amorphous variety, especially if it contains water, also dissolves in alkaline carbonates of the hot Icelandic springs, which, on exposure to air, deposit this substance, the alkaline silicates being decomposed by the atmospheric carbonic acid, while silica and an alkaline carbonate are formed. The occurrence of silica in these springs was observed as long ago as 1794 by Black, but even before that date Bergman had shown that small quantities of silica were contained in solution in the water of many springs."

Professor Hilgard has shown that silica is present in the waters of the springs of California, without saying in what form it is present, only as silica. And this is the statement of writers generally. "Stannic acids" are generally held responsible as the dissolving matter. But I think I will show that the shells of bacillariaceæ are not always silica, and that they are soluble in rain water, which is not pure water.

The rain falls as pure water, but it come into contact with the air, which is a mixture, not a compound, of nitrogen, oxygen, and argon, with various other substances, as carbonic anhydride, sulphur, and so forth. It there changes to an impure solution of air, oxygen, argon oxide (?), carbonic acid, and other things, but mostly ammonia. This was demonstrated by Schönbein over 30 years ago as a means by which the nitrogen goes to the plant life and afterward to the animal life of the globe.

Now ammonia in solution can dissolve silica which it finds in the soil, introduced there by the disintegration of the rocks. Silica is common in nearly all the rocks. It is pulverised very finely and just in the state to dissolve in alkaline (ammonia) solution. Silica pulverised and silica in the form of the shells of bacillariaceæ can be very readily dissolved in rain water, and also in all kinds of potable water. We have only to place some infusorial earth, which is the shells of bacillariaceæ, on a filter and pass potable water through it to find it dissolves very readily.

But the shells of bacillariaceæ are not always composed of silica. They may most commonly be composed of amorphous silica, most readily soluble in spring water. But they are commonly, as is seen in lacustrine sedimentary deposits, made up of clay, aluminium silicate, also readily soluble. They may sometimes consist of iron silicate, and most commonly of all the bacillariaceæ do not secrete all silica or a silicate at all, but their shells are made up of a compound resembling cellulose.

This I have found out by washing the shells in filtered spring water to see if I can wash them clean and mount them on a slide to make microscopic objects. I have found, to my sorrow, that they readily dissolve in fresh spring water, and I thought that the solubility of silica in water must be known to account for its presence in the soil, in spring water, and in the fossils of the earth.

I wish this communication to pass as a statement of the solubility of the shells of bacillariaceæ, and spongiæ, and radiolarie which are present in the infusorial earths and soundings.

HELIUM AND THE GAS X (?).

By R. M. DEELEY.

THE fact that three such experienced spectroscopists as Professors Runge and Paschen, and Mr. Norman Lockyer, should maintain that what has hitherto been regarded as helium is really a mixture of at least two elemental gases, should not be lightly passed over, even though the evidence may not be regarded as very satisfactory.

The reference made to this possibility in my short communication to the CHEMICAL NEWS of December 20th last, might be regarded as an indication that I considered that there is no place in the periodic system for another element of small atomic weight. Upon such a point the periodic law does not throw much light; for although the elemental gas X may exist it could not have been predicted.

Periodic tables, among which may be included Mendeleeff's, are generally so drawn up that if we were to regard each of their unoccupied spaces as indicating the existence of an unknown element, we should be compelled to regard our list of elementary substances as being still very incomplete. Some are satisfied that many of these spaces do not necessarily indicate that elements

TABLE I.

X	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	H
He	Li	Be	—	—	—	—	—	—	—	—	—	—	—	B	C	N	O	F
A	Na	Mg	—	—	—	—	—	—	—	—	—	—	—	Al	Si	P	S	Cl
—	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	
—	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	
—	Cs	Ba	La	Ce	Di	—	—	—	—	—	—	—	—	—	—	—	—	
—	—	—	Yb	Ta	W	U	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—	
—	—	—	—	Th	—	—	—	—	—	—	—	—	—	—	—	—	—	

TABLE II.

X	H	He	Li	Be	B	C	N	O	F	A	Na	Mg	Al	Si	P	S	Cl
?	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
?	Rb	Sr	Y	Zr	Nb	Mo	?	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
?	Cs	Ba	La	Ce	Di	?	?	?	?	?	?	?	?	?	?	?	?
?	?	?	Yb	?	Ta	W	?	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	?	?
?	?	?	?	Th	?	U	?	?	?	?	?	?	?	?	?	?	?

remain to be found for them, whilst others get out of the difficulty by asserting that such elements do exist, but say that they are never likely to be found.

In arranging the elements in tabular form I have endeavoured, whilst following the periodic theory of classification implicitly, to leave as few blanks as possible. I should, however, like to point out that, without doing any violence to Tables I and II (CHEMICAL NEWS, p. 297, December 20th, 1895), room can be found in the periodic system for at least one more element of small atomic weight. The altered arrangement is given in the accompanying tables.

In Table I. He is placed before Li, A before Na, and the new gas X at the commencement of the line at the extreme end of which is H. In Table II. X is the only element of the first column, and has an atomic weight less than that of H. This gives some support to the contention that there are spaces for elements between Cl and K, Br and Rb, &c.; but places such elements among the alkali metals instead of among the odd series elements. It also agrees with the reasoning of Professors Runge and Paschen, who state that the hypothetical gas X probably has a smaller atomic weight than helium. They also regard its spectrum as placing it among the alkali metals.

Making the order—

H	X	He	Li
?	K	Ca	Sc
?	Rb	Sr	Y

does not appear to be quite so satisfactory.

ON THE WAVE LENGTH OF THE D_3 HELIUM LINE.*

By A. DEFOREST PALMER, Jr.

OWING to the recent increased interest in the wave length of the helium lines due to the discovery of terrestrial helium, I have been led to calculate some observations on the D_3 chromosphere line carried out by myself at the Physical Laboratory of the Johns Hopkins University during February and March, 1893.

The measurements were made on the large fixed telescope spectrometer used by Dr. Louis Bell (*Amer. Journ. of Science*, vol. xxxv., p. 265) in his determination of the absolute wave length of the D solar lines, with a plane speculum metal grating having about fourteen thousand lines to the inch and five inches of grating space. The telescopes of this instrument are 16.4 c.m. clear aperture and about 2.5 metres focal length; and with the grating used I obtained good dispersion and excellent definition in the first spectrum to the right of the normal to the

grating. All the observations were made in this spectrum on account of its superior definition.

An image of the sun about 1 c.m. in diameter was formed on the slit of the instrument by aid of a large Foucault heliostat, and an achromatic lens of about four inches aperture. Appliances were provided for moving the image laterally across the slit, and, by means of a total reflecting prism, for turning it about the direction of the beam as an axis to bring any desired point of the limb over the slit.

The D_3 line appeared only when the sun's image was tangent to the slit, and then as a bright but very short line in the centre of the field of view vertically considered. Its definition and intensity were found to vary greatly from day to day, and for different points on the sun's limb. In general, when a solar prominence lay across the slit the line was very broad and intense, but the definition of its edges was poor, thus rendering it impossible to set the cross hairs on it with accuracy. The best combination of intensity and definition was obtained by avoiding prominences and working only on very clear days.

The observations were made by the ordinary microscopic method, the D_3 line being compared with the best solar standard lines in the field of view. The wave lengths of these standard lines, as taken from Professor Rowland's "Table of Standard Wave Lengths" (*Astr. and Astro-Phys.*, vol. xii., p. 321, and *Phil. Mag.*, V., vol. xxxvi., p. 49) were—

Fe	5916.475	Fe	5862.580
Fe	5914.384	Fe	5859.810
Fe	5905.895	Ba	5853.903
Na.D ₁ ..	5896.154	Average value	5887.028

Seventeen series of measurements were made, in each of which equal numbers of observations were taken on diametrically opposite points of the sun's limb in order to eliminate the effect of rotation.

The wave length of D_3 was calculated from each of these series by Professor Rowland's method of interpolation, on the assumption that, for the space used, the spectrum was essentially normal. The average of the seventeen values thus found gives

$$5875.939 \pm 0.006$$

for the wave length of the D_3 line, the probable error being calculated from the deviations of the several values from the mean in the usual manner.

To test the accuracy of the observations and method of calculation, the wave length of the mean line was computed from the observations and found to be 5887.027, a value which differs only by 0.001 from the average of the wave lengths of the standard lines used, 5887.028.

I am indebted to Professor H. A. Rowland and Dr. J. S. Ames for permission to use apparatus and for suggestions, and to Mr. W. S. Day for aid in making the observations.

* From the *American Journal of Science*, vol. 1., November, 1895.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 7.)

The Method of Ascertaining whether Chlorine be present or no in the Oxygen Liberated during the Dissociation of Chlorate and Perchlorate of Potassium by the Action of Heat.

THE research on the presence or absence of chlorine in the oxygen liberated during the dissociation of chlorate and perchlorate of potassium is one of a most delicate nature. As a matter of fact, the oxygen given off is always cloudy, and it generally contains chlorate, perchlorate, and chloride of potassium. In addition to this, the strong smell of ozone may lead one astray. I have only succeeded in my efforts by working in a well polished platinum retort. When one decomposes chlorate or perchlorate in a glass retort, even when annealed, there is always chlorine present. In order to completely free the oxygen from the potassic compounds which make it hazy, I used asbestos packing, such as I used when analysing the oxygen produced from chlorate, when decomposing this salt by the action of heat.*

The apparatus I used was arranged as follows:—I fitted the long neck of the platinum retort, filled with the potassic salt to be separated, and which had been previously washed, as far as possible into a large glass tube, 50 c.m. long. On the other end of this tube another tube, 5 m.m. inside diameter and bent to a slight obtuse angle, was fused; at this end there was a cylinder, almost the same diameter as the large tube, filled with pumice-stone which had been calcined after being soaked in concentrated sulphuric acid. Above this cylinder of pumice-stone was a pile of strongly heated asbestos felt, 25 c.m. high, and so packed as to allow the oxygen to filter freely, whilst stopping the saline dust.

The bent tube, fused to the large tube into which the neck of the platinum retort was fitted, was connected with one of the two holes in a glass plug, 8 c.m. in diameter, ground into a glass flask, containing a platinum dish one third full of water saturated with absolutely pure ammonia. This tube reached nearly to the surface of the ammoniacal liquid.

To the other hole in the plug was fitted a tube bent at an acute angle, communicating, by means of a rubber tube, with a Liebig apparatus containing a moderate quantity of pure water. The free end of the Liebig tube was in communication with a water-pump, which could be worked as slowly or as quickly as one wished.

Since the neck of the platinum retort, though reaching very far into the large tube, 50 c.m. long, did not completely fill the opening, the inner atmosphere could escape, and the outer atmosphere could penetrate inside, according as the inside pressure was greater or less than the outside pressure.

Profiting by experience, I regulated the aspiration so as to have constantly an *excess of pressure inside the apparatus*. To attain this result, I was guided by the smell of ozone, which is produced at the place where the neck of the platinum retort enters the tube; one could even detect an evolution of saline fumes at this part, when the dissociation of the potassic salt took place too rapidly for the amount of gas drawn through the apparatus.

I found I was obliged to adopt the above-described apparatus, and especially to use a platinum vessel to hold the concentrated solution of pure ammonia, because it is impossible to leave this solution in an ordinary glass vessel without the glass being attacked and sensibly dissolved.

For instance, if one evaporates in a platinum dish a concentrated solution of ammonia, which has been left for several hours in a glass beaker, one gets a white, strongly alkaline residue, made of silicate of calcium and sodium; and when the dissolved ammonia contains a very small quantity of chloride of ammonium, it is so far decomposed that the white residue does not contain any traces of it, and its chlorine is in the form of chloride of calcium and sodium.

When dissociating chlorate and perchlorate of potassium in the apparatus I have just described, by means of a well-regulated temperature, one sees these varying facts, according as the salts are absolutely pure, or contain iron, manganese, copper, silica, or silicates.

Do these salts bring the impurities mentioned above? as is the case with chlorate made by simple successive crystallisations in pure water, whilst the temperature of the melted chlorate is so high that the platinum retort emits the singing noise always heard during the dissociation of salt and the liberation of oxygen, when the gas, penetrating into the ammoniated atmosphere, *makes from the beginning to the end of the decomposition white fumes*, of which a part only dissolves in the ammonia in the platinum vessel; the remainder is carried off by the current of gas through the Liebig apparatus, so as only to be partly dissolved in the water it brings.

When evaporating ammonia, over which oxygen has passed, on a water bath in the covered platinum dish, there remains a white residue, quite *volatile* at a low temperature, and displaying *all the properties of chloride of ammonium*.

The water used to wash the gas, having been saturated with nitric acid, was clouded by the addition of a few drops of a 10 per cent solution of nitrate of silver.

Thus, as I demonstrated in my "Researches on the Reciprocal Ratios of Atomic Weights," there is no doubt as to the presence of chlorine in the oxygen liberated during the dissociation of chlorate of potassium containing impurities in the salt, made by successive crystallisations in pure water. As the liberation of chlorine shows itself until the end of the operation, it necessarily follows that the decomposition of perchlorate made during the dissociation of chlorate must also take place with the liberation of chlorine. I have elsewhere stated that siliceous perchlorate of potassium, when decomposed by heat, yields oxygen mixed with traces of chlorine. The facts are quite different when substituting *pure* chlorate and perchlorate for even slightly siliceous chlorate.

When *pure* chlorate is decomposed by the action of heat, either slowly or more or less quickly, the oxygen drawn through the asbestos felt, on coming in contact with ammonia, suddenly forms a *very slight haze*, probably due to the action of the ozone in the oxygen on ammonia, which, according to Carius, makes nitrite of ammonium, but never a smoke such as is seen when chlorine mixed with oxygen comes in contact with ammonia gas.

So long as the aspiration is not great, the oxygen reaches the Liebig apparatus quite transparent, and passes through it without producing the slightest haze.

I evaporated on a water bath, in a covered platinum dish, the ammonia across which had passed oxygen from the dissociation of:—1st, 60 grms.; 2nd, 100 grms.; 3rd, 150 grms. of pure chlorate of potassium; 4th, 57 grms. of pure perchlorate of potassium. I effected the decomposition of the pure perchlorate under the same conditions as the chlorate, at the request of M. Berthelot. During all four trials the evaporation was completed without leaving any residue. The surface of the platinum dish was washed with pure water; this was found to be neutral to litmus paper, and remained quite clear after the addition of five drops of a 10 per cent solution of nitrate of silver, and remained *clear and colourless* after being exposed to direct sunlight—a phenomenon only seen so long as the liquid contains no trace of chloride of silver.

The water in the Liebig apparatus, through which the oxygen had passed, having been neutralised by nitric acid,

* "R  cherches sur les Rapports R  ciproques des Poids Atomiques" (*Bulletins de l'Acad  mie Royale de Belgique*, 2e S  r., t. x., p. 109).

and having then had some nitrate of silver added, kept quite clear in all four experiments; it remained clear and colourless after a long exposure to direct sunlight.

It is therefore proved that *pure* chlorate and perchlorate of potassium can be dissociated in a *pure* and *polished* platinum dish without liberating a trace of chlorine. I have further found that the chloride of potassium made at the same time is *absolutely neutral* to colour tests. These two facts, which I was unable to discover for more than a third of a century, prove the constancy of the ratio between the weights of chlorine and potassium in chlorate, perchlorate, and chloride of potassium, and fully confirm the conclusions I drew from the action of sulphurous acid on chlorate, bromate, and iodate of silver, made under normal conditions. It was with the hope of being able to show the accuracy of the law of definite proportions, without having resource to chemical action and weighings, that decided me to devote much time and great care to finding out, whether or no, chlorate and perchlorate could, *by the action of heat alone*, be changed into chloride, without liberating an appreciable trace of chlorine.

Spectroscopic Study of Potassium.—Character given to Flames by Compounds of Potassium.

The Luminous Spectrum of Potassium.—Chemists state that potassium compounds give a purplish-blue colour to the envelope of the flame of a well-made Bunsen burner. I must say I was surprised to find that *chlorate* and *perchlorate* of potassium, from which I had eliminated all solid compounds and sodium, when put into the outer part of this flame on a loop or spiral of fine platinum wire, gave it a *pale* or *sky blue* colour, and *chloride* of potassium a *deep blue* colour. These colours were also seen in a pure hydrogen flame, and in a hydrogen and air, oxyhydrogen, and oxy-coal gas blowpipe flames.

Experiments most carefully conducted, using the purest potassic compounds, have convinced me that the blue tint is stronger as the mass of potassium is *greater* at a similar temperature, and it becomes *fainter* as the temperature is raised, when the mass is the same. Beyond the fusing point of platinum the colour of an oxyhydrogen blowpipe flame charged with potassium is very pale blue; it is even paler than incandescent hydrogen; thus one is tempted to ask whether the vapour of potassium compounds is still coloured when raised to the very highest temperature, such as the fusing point of iridium.

Spectrum analysis of potassium *flames*, coloured light or dark blue, shows the spectrum of potassium compounds, as it was described and measured by M. Lecoq de Boisbaudran in 1874, and in 1875 by M. Bunsen, in his memoir "*Spektal-Analytische Untersuchungen*," that is to say, it consists of a *red* line, a *pale red* band, and a very faint *purple* line. *The sodium D line is not present.*

Notwithstanding that I had seen the pale red band, mentioned by M. Bunsen and Lecoq de Boisbaudran as being due to potassium, I always had doubts as to the origin of this band. In fact, when making a spectrum analysis of a potassic hydrogen flame, at a temperature where the gas no longer shows a *continuous spectrum*, and shutting out rays from the support, and using a sufficiently narrow slit, the spectrum consists of an *absolutely dark band* in which only the *red* line at 21.5 divisions on the micrometer scale of my spectroscope, corresponding to 17.4 on that of M. Bunsen, and the *purple* line at 140.50 on my scale, corresponding to 153.5 on that of M. Bunsen, are visible.

However narrow the slit might be, whenever we make a spectrum analysis of an incandescent hydrogen flame in which a potassium compound has been volatilised, the spectrum is *continuous*, showing the red line at 21.5 on my spectroscope, corresponding to 17.4 on that of M. Bunsen, and the purple line at 141.5 on my spectroscope, corresponding to 153.5 on that of M. Bunsen. *In both cases I have noticed the absence of the red band and the sodium line.*

I was able to show that the flames of pure chlorate and

perchlorate of potassium were *pale blue*, and that the faint red band and the sodium D line were absent from the potassium spectrum during the months of November and December, 1878, December, 1880, and November and December, 1882 and 1883. M. Rommelaere, who assisted me in this work noticed the same facts.

To obtain the double condition, *i.e.*, the flame coloured light blue, and the sodium line not present, there are required—(1st) the air very pure; (2nd) nascent potassium compounds.

The method which gave me the best results consisted in plunging a fine platinum wire loop, covered with iridium, previously heated to whiteness to drive off sodium brought by the air, into a saturated and boiling solution of the potassic compound, made when sheltered from atmospheric dust, and in putting this loop at once into the outer part of an oxyhydrogen flame or blowpipe, with an excess of hydrogen.

If the salts adhering to the platinum loop, or the bulk of it, are kept under a bell-jar in contact with air, after a few hours, and sometimes after half an hour, they show, on spectrum analysis, unmistakable signs of the presence of sodium absorbed from the air, and they colour flames a *purplish blue*. Chlorate, perchlorate, and chloride of potassium, which were quite free from sodium at the time of their preparation, when put into bottles with ground-glass stoppers, and opened from time to time, and kept for six months in a closed cupboard, showed the sodium line, on spectrum analysis, as strongly as chlorate, perchlorate, nitrate, and monopotassic tartrate, which had been purified by ten successive crystallisations under cover from atmospheric dust, and they coloured the hydrogen flame a purplish blue. *The contamination of potassium compounds by atmospheric sodium is enough to cause them to sensibly colour a flame yellow if the action has lasted long enough.*

Potassium salts then resemble platinum, silver, carbon, &c., which also absorb sodium from the air. The experiments I describe further on show that it is just the same with all the bodies on which I have carried on my investigations.

When one tries to reproduce the phenomena I have just described, in air contaminated by mineral and organic dust in suspension, as is nearly always the case in places where work is carried on, the introduction of the purest potassium compounds gives a varying colour to the flames, which are frequently greenish yellow at first, changing to strong violet after a few moments, and keeping this colour until the potassic salt has completely disappeared. In this case the sodium line, and *often an incomplete calcium spectrum*, is *always* seen accompanying the characteristic potassium lines. The calcium spectrum is more marked, when some hydrogen which has been impregnated with hydrochloric acid by passing through a saturated solution of the same, is introduced into the potassic flame.

The colour given by potassium compounds to coal-gas or pure hydrogen, burning in an excess of air, is then pale blue, deep blue, or violet blue, according to the state of the air and the potassic compounds.

I mentioned above that the very purest of these compounds, when kept for some time in closed glass vessels, with emery-ground stoppers, but opened from time to time, give unmistakable signs of the presence of sodium. I ought to add that, in this case, they give to the flame that violet colour looked upon by all chemists as a distinctive characteristic of potassium compounds. I have tried to find the reason for this difference in colour. Having frequently noticed the formation of an incomplete calcium spectrum during the production of the violet flame, I thought at one time that this colour was due to the presence of traces of calcium in the potassium compound, and in truth the complete elimination of calcium is very difficult. But I soon found I was not able to detect the calcium spectrum, or any of the characteristic lines of this metal, in the spectrum of violet flames con-

taining a given potassium compound. One day I volatilised five grms. of chloride of potassium made from pure perchlorate in an oxyhydrogen blowpipe; after some seconds, the flame, which was first deep blue, then light blue, became intensely violet. During the few minutes occupied in volatilisation, I watched the spectrum, and although I was obliged to raise the temperature in the first place so high that I melted the concave sheet of platinum in places, and in the second place I used a cup of pure iridium containing a hollow cone of this metal, heated almost to its fusing point, I was unable for a single instant to see the calcium spectrum or even any one of its characteristic lines in the very bright potassium spectrum.

A part of the same chloride of potassium made from perchlorate, when volatilised several months afterwards, coloured the flame blue throughout the experiment, and the colour became fainter as the temperature was raised; this colour never passed the azure tint shown at the same time by an oxyhydrogen blowpipe flame free from all traces of potassic vapour. Thanks to the exceptional purity of the air on this occasion, I was able to repeat the experiment twice, with the same result.

Unless the potassium rays masked the weak calcium rays, which is not impossible when considering the analogous facts noted, I can only attribute the difference in colour, given to the same flame by the same chloride, to sodium brought by air currents.

I give the facts as they appear from my own observations, thoroughly checked by myself and by other persons who have witnessed them.

Whatever may be the cause of the variation in the colouring of flames by pure potassic compounds, the fact, the investigation of which has been the object of my chemical and spectroscopic researches on potassium, can be no longer doubted. I have found beyond a doubt that it is possible to get potassium compounds which, when put into flames, give no trace of the double D sodium line, and that at the very highest temperatures of hydrogen or coal-gas burning in pure oxygen. The double D line is only seen in the potassium spectrum, when the air, or the compound being examined, contains sodium as an impurity, as is the case with nitrate of potassium, which I could not obtain without a slight trace of sodium, and which coloured a hydrogen flame pale blue tinged with violet.

My researches enable me to state these facts in a positive formal manner.

The spectra of chlorate, perchlorate, chloride from perchlorate, chloride from chlorate, and chloride from chloroplatinate of potassium are identical; they consist of either a dark or bright continuous spectrum, both marked by two lines, according as the spectrum analysis is made of a potassium flame in which the hydrogen either is not or is made incandescent. In the latter case the illumination of the spectrum is partial or total, according as the compound is put and the analysis made outside or inside the inner cone of an oxyhydrogen or oxy-coal-gas blowpipe.

Potassium then behaves as a body distinct from sodium; it is not reducible to sodium by heat. Much evidently depends on the conditions under which researches can actually be carried on.

(To be continued).

Action of Chlorocarbonic Oxide upon some Derivatives of Sulphonic and Sulphinic Acids.—P. Tischendorf.—The author has attempted to extend the formation of urea from chlorocarbonic oxide and ammonia to some ammoniacal derivatives of aromatic sulphoacids. He has to this end examined the behaviour of phenylsulphonamide (melting-point 148°), *p*-tolylsulphonamide (melting-point 107°), phenylsulphonphenylamide (melting-point 134°), and para-tolylsulphonphenylamide (melting-point 99°), but in only two cases has he obtained the results expected.—*Zeits. f. Prakt. Chem.*

THE PREPARATION OF PERCHLORIC ACID AND ITS APPLICATION TO THE DETERMINATION OF POTASSIUM.*

By D. ALBERT KREIDER.

(Concluded from p. 9).

In applying perchloric acid, thus prepared, to the determination of potassium according to the treatment suggested by Caspari (*loc. cit.*), very satisfactory results were obtained. Briefly, the method is as follows:—The substance, free from sulphuric acid, is evaporated to the expulsion of free hydrochloric acid, the residue stirred with 20 c.m.³ of hot water and then treated with perchloric acid in quantity not less than one and one-half times that required by the bases present, when it is evaporated with frequent stirring to a thick syrup-like consistency, again dissolved in hot water, and evaporated with continued stirring till all hydrochloric acid has been expelled and the fumes of perchloric acid appear. Further loss of perchloric acid is to be compensated for by addition of more. The cold mass is then well stirred with about 20 c.m.³ of wash alcohol—97 per cent alcohol containing 0.2 per cent by weight of pure perchloric acid—with precautions against reducing the potassium perchlorate crystals to too fine a powder. After settling, the alcohol is decanted on the asbestos filter and the residue similarly treated with about the same amount of wash alcohol, settling and again decanting. The residual salt is then deprived of alcohol by gently heating, dissolved in 10 c.m.³ of hot water and a little perchloric acid, when it is evaporated once more with stirring until fumes of perchloric acid rise. It is then washed with 1 c.m.³ of wash alcohol, transferred to the asbestos, preferably by a policeman to avoid excessive use of alcohol, and covered finally with pure alcohol: the whole wash process requiring about 50 to 70 c.m.³ of alcohol. It is then dried at about 130° C. and weighed.

The substitution of a Gooch crucible for the truncated pipette employed by Caspari will be found advantageous; and asbestos capable of forming a close, compact felt should be selected, inasmuch as the perchlorate is in part unavoidably reduced, during the necessary stirring, to so fine a condition that it tends to run through the filter when under pressure. A special felt of an excellent quality of asbestos was prepared for the determinations given below, and seemed to hold the finer particles of the perchlorate very satisfactorily.

A number of determinations made of potassium unimixed with other bases or non-volatile acids are recorded in the following table:—

KCl taken. Grms.	Volume of filtrate. C.m. ³ .	KClO ₄ found. Grms.	Error on KClO ₄ . Grms.	Error on KCl. Grms.	Error on K ₂ O. Grms.
0.1000	54	0.1851	0.0008—	0.0004—	0.0003—
0.1000	58	0.1854	0.0005—	0.0002—	0.0002—
0.1000	51	0.1859	0.0000	0.0000	0.0000
0.1000	50	0.1854	0.0005—	0.0002—	0.0002—
0.1000	48	0.1859	0.0000	0.0000	0.0000
0.1000	52	0.1854	0.0005—	0.0002—	0.0002—

Considerable difficulty, however, was experienced in obtaining equally satisfactory determinations of potassium associated with sulphuric and phosphoric acids. As Caspari has pointed out, the sulphuric acid must be removed by precipitation as barium sulphate before the treatment with perchloric acid is attempted, and unless the precipitation is made in a strongly acid solution, some potassium is carried down with the barium. Phosphoric acid need not be previously removed; but to secure a nearly complete separation of this acid from the potassium, a considerable excess of perchloric acid should be

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xlix., June, 1895.

left upon the potassium perchlorate before it is treated with the alcohol. When these conditions are carefully complied with fairly good results may justly be expected. Below are given a number of the results obtained.

Compounds taken. Grms.	Vol. of filtrate. C. m. s.	KClO ₄ found. Grms.	Error on KClO ₄ . Grms.	Error on KCl. Gims.	Error on K ₂ O. Grms.
KCl=0.10					
CaCO ₃ =0.13	50	0.1887	0.0028+	0.0014+	0.0009+*
MgSO ₄ =0.13	82	0.1875	0.0016+	0.0008+	0.0005+*
Fe ₂ Cl ₆ =0.05	80	0.1861	0.0002+	0.0001+	0.0001+†
Al ₂ (SO ₄) ₃ =0.05	80	0.1843	0.0016-	0.0008-	0.0005-†
MnO ₂ =0.05	92	0.1839	0.0020-	0.0010-	0.0006-†
HNa ₂ PO ₄ .					
H ₂ H ₂ O=0.40	60	0.1854	0.0005-	0.0002-	0.0002-†

In the last three experiments of the above table the amount of perchloric acid was about three times that required to unite with the bases present, and the phosphoric acid subsequently found with the potassium was hardly enough to appreciably affect the weight, although its absolute removal was found impossible.

The kindly direction and frequent advice of Professor F. A. Gooch during the investigation is gratefully acknowledged.

A VOLUMETRIC METHOD FOR LEAD ANALYSIS.

By ALFRED C. BEEBE,
Chemist to the Chicago and Aurora Smelting and Refining Company.

As I have found the existing volumetric methods for the analysis of lead more or less unsatisfactory, on account of the lack of a sharp characteristic end reaction, I have devised the following scheme, which combines accuracy with rapidity.

It depends upon titrating a solution of acetate of lead free from alkali salts by means of ferrocyanide of potassium, using a saturated solution of uranium acetate as an indicator. The end reaction, which is formed by adding a drop of the solution, being titrated to the uranium solution on a porcelain plate, is a delicate pink, changing, after standing some time, to brown. The ferrocyanide solution can be standardised with either lead sulphate or lead acetate. Eleven grms. of ferrocyanide in one litre of water will give about a 1 per cent solution. The uranium acetate solution should have a little free acetic acid in it, or the sharpness of the end reaction is affected.

The method for analysis is as follows:—Dissolve the substance to be analysed in nitric acid, using a little hydrochloric acid if necessary. When the decomposition is complete add sulphuric acid and evaporate till white fumes of sulphuric anhydride are given off. Dilute with water and cool. Add to the liquid its own volume of common alcohol and allow it to stand a short time. Filter and wash with hot water. Then wash the residue into about 50 c.c. of a cold saturated solution of ammonium carbonate with some of the carbonate solution. Stir frequently and vigorously for about 15 minutes. Filter, and wash both residue and filter very thoroughly with hot water. Dissolve the lead carbonate in hot dilute acetic acid. Cool and titrate with a solution of ferrocyanide of potassium.

Barium and calcium do not interfere with the results. Arsenic is eliminated by the method of treatment. Antimony compounds can be made soluble by the use of tartaric acid in the decomposition of the substance. Should iron, copper, or zinc be present, a very thorough washing of the lead sulphate will be necessary. If any substance is found to interfere seriously with the results, the copper and arsenic groups can be separated from their acid solu-

tion by means of sulphuretted hydrogen. The resulting sulphides can be dissolved in nitric acid and the regular method of analysis followed.

I have used the method as given above with excellent results. As, however, there are many artificial and natural products I have had no opportunity to try, I will regard it as a favour if other chemists will send me criticisms or suggestions concerning this scheme.—*Engineering and Mining Journal*.

ON THE PROLONGED ACTION OF LOW HEATING ON DETONATING GAS.

By VICTOR MEYER and WILHELM RAUM.

It is well known that in heat detonating gas is converted into water, whilst in the cold it remains unchanged. But whilst there is no doubt as to its condition in heat there prevail two opinions concerning its behaviour at common temperatures. The great body of chemists hold that it undergoes no reaction, whilst the majority of physical chemists are convinced that a formation of water occurs, but that the speed of the reaction is so small that it remains unperceived. For this assumption evidences are not wanting. For instance, the reaction becomes at once perceptible by katalysis, by the addition of platinum black, and attains a considerable rapidity. But it is probable that substances which act katalytically never introduce a reaction which previously does not exist, but merely increase its rapidity. That the reaction is not perceptible in the cold need not surprise us, since all experience in this region teaches us that the rapidity of chemical reactions decreases remarkably with a reduction of temperature. Theoretical considerations teach us the same. Hence it is probable that the reaction on descending from 500°—at which temperature it takes place with moderate rapidity—to the temperature of a dwelling-room, undergoes an enormous retardation, so that recognisable quantities of water would appear only in the course of centuries or of thousands of years.

Nernst has recently pointed out that it is not indifferent whether we consider a reaction as absolutely non-existent or as taking place with an immeasurably small rapidity.

An exact demonstration might be given by keeping detonating gas for a very long time and observing the appearance of a contraction. I have already shown that this phenomenon does not occur within the lapse of two years, and according to Berthelot the same result has been obtained in an observation continued for many years.

As time is wanting to extend the experiment for the necessary duration, we had to be contented with an approximate experiment based on the following consideration. We first ascertained the temperature at which, in common language, detonating gas no longer reacts, i.e., undergoes no change on observation for several days. This temperature we found at 300°; on heating specimens of detonating gas uninterruptedly to this temperature for 10 days, we could not observe any formation of water. Next, detonating gas was exposed to this temperature for a much longer time without interruption (65 days and nights). Setting out with the opinion that at temperatures which lead apparently to no reaction, still such a reaction would be manifested on extremely long heating, we expected that here a formation of water would appear. *This was in fact the case.* If, therefore, at 300°—which temperature shows no formation of water in observations of an ordinary duration—a reaction becomes manifest on a very protracted heating, the assumption seemed admissible at still lower temperatures, and that formation of water would be detected on a further prolongation of the experiment.

The performance of these experiments presented various technical difficulties, and did not prove so simple as we

* The residue showed phosphoric acid plainly when tested,
† Only traces of phosphoric acid found in the residue.

at first expected. The investigation was always effected according to the method described by Victor Meyer, Krause, and Askenasy (*Ann. der Chemie*, cclxiv., 85, and cclxix., 49). The specimens of detonating gas were heated in vessels sealed hermetically, and having capillary appendages of one-third m.m. internal diameter. The gas was prepared and electrolytically purified from ozone and dried over sulphuric acid. The usual precaution was observed of employing check bulbs, sealed under identical conditions, and preserved unchanged, in order, on opening the bulbs, to be independent of the state of the thermometer or barometer, was here employed. In the former investigations it was shown that the formation of water commenced very plentifully at 518° (vapour of P_2S_5), slowly in vapour of sulphur (448°), and scarcely perceptibly in mercurial vapour (350°). Our experiments showed that at the last temperature the quantities of water formed were not inconsiderable. We obtained in 50 hours 1.6 per cent; in 60 hours 1 to 1.6 per cent; in 120 hours 1.9, 1.6, 0.5, 0.7, 1.2 per cent.

The heating to 300° —particularly important for our purpose—was first undertaken in the vapour of diphenylamin (boiling point 305°). On heating a number of specimens for ten days we obtained no recognisable quantities of water. For a much more prolonged experiment diphenylamin seemed less convenient, as after some time it becomes resinified, and even in the above mentioned relatively brief experiment it had to be several times renewed. For prolonged experiments a metal bath was therefore used with a suitable regulator. During 65 days the temperature never rose more than 4° or 5° above 300° .

Of the six bulbs employed only three survived the experiment, whilst the remainder burst. The quantities of water produced in the former were respectively 9.5, 0.4, and 1.3 per cent.

We must further mention that we made an experiment by heating bulbs filled with detonating gas for 218 days and nights, without intermission, in a boiling water-bath. There was no perceptible formation.—*Berichte*, xvii., p. 2804.

TELLURIUM: ITS SEPARATION FROM COPPER RESIDUES, WITH NOTES ON SOME NEW REACTIONS.

By CABELL WHITEHEAD.

TELLURIUM, which a few years ago was classed as a rare metal, is now known to be distributed over a very wide area, not only in our western states, but also in the gold-producing states of the east. It occurs in the free state, and also combined with gold, silver, bismuth, and many other metals. In the state of Colorado, tellurium is found in combination with gold and silver to such an extent that the ores in many districts are rendered unfit for amalgamation, and smelting and chlorination has to be resorted to. The separation of silver and gold from low grade telluride ores is a problem which, up to the present time, has baffled the skill of the metallurgists of the world. A few of the difficulties may be mentioned as follows:—Tellurides do not give up their gold to mercury, cyanide, or chlorine; they concentrate badly, a large percentage of the value being lost as slimes. They are difficult to roast, on account of their low melting-point, and the loss of gold during the removal of the tellurium. The usual course is to smelt this class of ore either with lead or copper ores. It is to the latter method I will call especial attention in this paper.

In order to work the copper ores of the west economically, they are smelted with gold- and silver-bearing ores, which act as flux, and also enrich the matte produced to a point where the cost of refining the copper is more than covered by the value of the precious metals contained. In this way large amounts of tellurium enter the

matte. These mattes are Bessemerised in the west, and copper brought east to be refined by electrolysis. It contains from 98.5 to 99.5 per cent copper, about 100 ounces of silver, and 3-10ths ounce of gold per ton. The impurities are arsenic, antimony, lead, bismuth, tellurium, and selenium. The average amount of tellurium is not far from 0.04 per cent, or 0.8 of a pound per ton. With the possible exception of the native copper of Lake Superior, it is doubtful if any copper produced is free from tellurium; this is certainly true of that from sulphide ores. I have already described a method for estimating the tellurium under these circumstances (*Journ. Amer. Chem. Soc.*, xvii., 280, 1895).

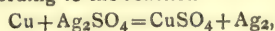
The electric refining of such copper is carried on at Anaconda, and at the Boston and Montana Copper Co. works at Great Falls, Montana; the Baltimore Electric Refining Co., Baltimore, Maryland; the Bridgeport Copper Co., Bridgeport, Conn.; and the Ansonia Refining Co., Ansonia, Connecticut; the Central Falls Electric Refining Co., Central Falls, Rhode Island; the Washburn and Moen Co., Worcester, Mass.; and perhaps others.

In the Hayden process a bath of dilute copper sulphate, acidified with sulphuric acid, is employed, in which is inserted an anode of rolled black copper and a cathode from a strip of pure copper, each being connected with the electric generator, while disconnected plates of black copper are suspended in the bath between the two electrodes. When the current is on, solution takes place, not only at the anode but on all the disconnected plates interposed between the electrodes, and, what is more interesting, this solution takes place on those surfaces of these plates which face the negative electrode, while the deposition of the pure copper takes place on the surface of the adjacent plate which faces the positive electrode. When the copper goes into the solution in its bath, small amounts of some of the impurities in the copper enter into solution with it, but the greater portion remains either in the metallic state or are converted into oxides or basic salts which fall to the bottom of the bath, where they form a black slimy residue.

The commercial refining of these residues is carried out as follows:—

After screening out the coarser copper, the slimes are boiled with a 20 per cent solution of sulphuric acid in a lead-lined tank by live steam, air being drawn in with the steam by means of a peculiar injector. During this boiling, practically all of the antimony, arsenic, and bismuth salts, together with copper in the oxidised condition, and that small portion of metallic copper which has been oxidised by the injected air, go into solution.

After about one hour's boiling, a solution of silver sulphate is run in and steam applied for some minutes, whereby, according to the reaction—



the metallic copper still remaining is rapidly and completely converted into copper sulphate. Any excess of silver sulphate is removed by the addition of a fresh portion of slimes, when the solution is drawn off and the residue washed until free from copper salts. This residue, which has now lost the slimy adhesive properties which characterised it, and which consists of gold, silver, tellurium, and lead sulphate, is pressed on a filter-press. The pressed cakes are dried in an oven and then melted in a furnace, having a bed made of Portland cement, which is so arranged that a blast may be turned on. This quickly removes all but a trace of the lead present, together with portions of the tellurium and selenium.

The resulting bullion is poured into shoe-bars, weighing about 300 ounces each; it is about 950 fine in silver, and 10 parts of gold. When cool these bars are dissolved in hot sulphuric acid, in a cast-iron kettle; and when solution is complete the liquid is allowed to cool and settle for several hours, during which the gold falls to the bottom and the tellurium crystallises out in white lustrous

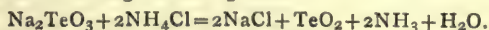
crystals of tellurous oxide. The first portion of the clear liquid is drawn off and precipitated by metallic copper, and the silver melted into bars 990 fine. The remainder is used in treating a fresh portion of the slimes.

The gold and the tellurous oxide are allowed to accumulate in the kettle until several hundred ounces are at hand, when they are removed and washed with dilute sulphuric acid and water, to remove silver, copper sulphate, and tellurous oxide, and afterwards boiled in a small kettle with concentrated sulphuric acid, to remove the remaining portion of silver and tellurium. When cool, and the gold has settled, the acid is again drawn off and the residue washed until free from tellurium and silver sulphates. The gold is now melted with borax and nitre, by which any remaining traces of lead and tellurium are oxidised and slagged off, leaving fine gold, over 990 fine, the impurity being silver.

The washings from the gold residue contain the tellurium as tellurous oxide or tellurous sulphate. The tellurium may be obtained from these in two ways, after the removal of the silver as chloride. First, by precipitation with copper; second, by passing sulphur dioxide through the solution. It is better to use the first method, as large quantities of sulphur dioxide are very disagreeable to handle, and as the tellurium thus precipitated in the presence of copper is not pure and requires a further treatment. The metal used in this work was produced by inserting bars of copper into the solution and boiling with steam, a precipitate of cuprous telluride being obtained as a black powder. This was dried and then boiled with a 5 per cent solution of sulphuric acid, to remove the copper which had been oxidised during the drying process. After filtering, the mass is again moistened with 5 per cent sulphuric acid, and subjected to atmospheric oxidation with frequent stirring, then boiled again with more sulphuric acid, and washed; this process is repeated until the copper is eventually very completely removed. Any copper left will combine with tellurium when fused, and cause loss. The residue is now dried, mixed with three times its weight of sodium carbonate and one-fourth its weight of charcoal, melted in a French clay crucible to quiet fusion, brought almost to a white heat, and the melt poured into a suitable mould. The cooled mass is crushed to a powder and the sodium telluride formed, dissolved out with boiled water; a great amount of heat is developed during the solution. The solution thus produced, which possesses a rich port-wine colour, is filtered off, and the tellurium precipitated in the metallic state, by the passage of a current of air, as a fine grey powder, looking not unlike finely-powdered galena. The tellurium is filtered and boiled with dilute hydrochloric acid, to remove traces of iron, alumina, &c., washed and boiled for several hours, with a concentrated solution of potassium cyanide, which removes selenium and most of the gold present. After drying, the tellurium is melted, without flux, in a French clay pot; the fine particles are made to run together by stirring; only a low temperature is necessary, and the loss by volatilisation is small. The metal still contains traces of impurities, the chief of which is gold. This would indicate that sodium telluride is a solvent of metallic gold, but this has not yet been proven. The tellurium is further purified by distillation in hydrogen gas.

New Reactions of the Salts of Tellurium.

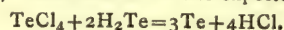
If to a solution of the sodium or potassium tellurite is added a solution of an ammonium salt, such as the chloride or nitrate, a white precipitate is thrown down, which on boiling becomes granular.



A small amount of tellurium dioxide, or a metal which can be precipitated by sulphur dioxide, remains in solution. It is the intention of the writer, as soon as possible, to examine and compare the properties of the metal

from this fractional precipitation. While it is probable that tellurium oxide is slightly soluble in the alkali salts formed, which would explain incomplete precipitation, in view of the growing belief in the compound nature of tellurium, this reaction is deemed worthy of further investigation.

In an effort to purify tellurium, based upon the well-known property of hydrogen telluride of precipitating many of the metals from solution, the following reaction was observed, in addition to the one expected.—



By passing this gas for some time into a solution of tellurium chloride, made slightly acid with hydrochloric acid, there was obtained a precipitate of tellurium and tellurides and a solution, from which sulphur dioxide threw down a precipitate of tellurium. After distillation in hydrogen, I propose to determine the atomic weight of this purified metal.

When potassium ferrocyanide is added to tellurium chloride no change is observed at first, but after a few hours Prussian blue is formed in large quantities.

Aluminum Telluride.

Tellurium when heated with aluminum combines with explosive violence, forming a chocolate-coloured, difficultly fusible compound, having the following composition by analysis:—

	Per cent.
Aluminum	12.78
Tellurium	87.22
	100.00

This corresponds closely to the formula Al_2Te_3 , which requires—

	Per cent.
Aluminum	12.58
Tellurium	87.42
	100.00

The violent chemical action attending its formation, joined with the fact that its composition remains constant, even in the presence of a large excess of aluminum, would indicate a true chemical combination and not an alloy, in the accepted sense. It is hard and brittle, can be easily ground to powder. When exposed to moist air it is slowly decomposed with the liberation of hydrogen telluride. When thrown into water, hydrogen telluride is rapidly given off according to the following reaction:— $\text{Al}_2\text{Te}_3 + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{Te}$, which corresponds to the well-known sulphur reaction $\text{Al}_2\text{S}_3 + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{S}$. While comparing these two reactions, it may be noted that hydrogen telluride is much more easily decomposed by oxygen than hydrogen sulphide. For example, in treating aluminum telluride with water which has not been boiled, fully one-half of the tellurium remains as metal:— $\text{H}_2\text{Te} + \text{O} = \text{H}_2\text{O} + \text{Te}$. When treated with 95 per cent alcohol no reaction takes place, even on boiling. This would seem to be the best one of the tellurides from which to make the organic salts, as it does not decompose in the air so quickly as the alkali tellurides.

Separation from Copper by the Electric Current.

Tellurium is easily deposited by the current either from acid or alkaline solutions; even the feeblest current throws out the metal, but unfortunately not in the reguline state.

It has been found possible to separate tellurium from copper by adding an excess of sodium hydroxide and about 3 grms. of potassium cyanide for each grm. of copper present. With this solution, a current such as is used for depositing copper will throw out all the tellurium present, as a black non-adherent precipitate. After twelve hours the tellurium is filtered off and weighed, either as metallic tellurium on a weighed filter or as tellurium dioxide. The solution is now made slightly acid

with sulphuric and the copper precipitated in the usual way. If the proper amount of potassium cyanide has been added, and the current has not been allowed to run too long, the tellurium is perfectly free from copper, and if the current is strong enough none of it will adhere to the cathode.—*Journ. Amer. Chem. Soc.*, vol. xvii., p. 849.

NOTICES OF BOOKS.

Gas Manufacture: The Chemistry of. A Practical Handbook on the Production, Purification, and Testing of Illuminating Gas, and the Assay of the By-products of Gas Manufacture. For the Use of Students, Chemists, and Gas Engineers. By W. J. ATKINSON BUTTERFIELD, M.A., F.C.S., Head Chemist, Gas Works, Beckton, London, E. With numerous illustrations. London: Charles Griffin and Co., Ltd. 1896. Pp. 375.

ENGINEERS have so completely possessed themselves of the supreme direction of gas-works that the outside public is apt to forget that we have here to do with an essentially chemical manufacture.

For this reason, among others, we must heartily welcome the appearance of the present work.

Among the numerous points that call for special notice we must mention the increase in the yield of ammonia from coal, effected by an admixture with lime before ignition. The effects of this addition (Cooper's patent) are promised subsequent consideration, but unfortunately we have not been able to meet with the passage.

The effects of high temperature in heating the retorts are duly considered. It is admitted that working at a low temperature yields an improved quality of gas at the expense of its quantity.

It is a serious consideration that the proportion of the deadly carbon monoxide in coal-gas may reach 9 per cent. Hence the possibility of explosions is not the only evil resulting from an escape of gas.

The use of water-gas for domestic purposes requires very great caution, as the proportion of carbon monoxide may reach 33 per cent of the total volume. According to O. Wyss, here quoted from the *Zeitschrift für Angewandte Chemie*, 10 per cent diffused in air renders it fatal to warm-blooded animals, man being included. We see no reference here to the process devised by Mr. Crookes for removing this constituent from water-gas. The Leeds accident cannot be forgotten: how the body of a man poisoned by water-gas was so saturated with carbon monoxide that alarming effects were experienced by the surgeons making the autopsy.

Acetylene, as a material for enriching coal-gas, is not free from objections. Its cost is under many circumstances practically prohibitive, and its toxic properties cannot be overlooked.

The standards of light are of great importance, and involve no small difficulty. The English normal candle, and indeed all normal candles, are untrustworthy. It is found that, however carefully prepared, they cannot be uniformly made to burn exactly 120 grms. of spermaceti hourly. Probably the pentane lamp of A. Vernon Harcourt will be ultimately recognised as the official standard. It emits a light of ten times the value of the standard candle.

The amyl-acetate lamp of F. von Hefner-Altenneck is somewhat similar in principle to the pentane lamp. It has to a considerable extent superseded the German standard paraffin candle. This candle is slightly superior in lighting power to the English normal candle. The German standard paraffin candle = 1.05 English normal spermaceti candle.

The French Carcel lamp is now round exactly equal to ten English normal spermaceti candles.

The standard of M. Violle is the light of a square centimetre of liquid platinum exactly at the solidifying point. It is here pronounced as "deliciously impractical." The surface of molten platinum is found to have small scum-like particles constantly floating over it, and these particles give far more light than the mass of metal itself.

It is admitted that some large provincial towns, especially in the North, are supplied with a richer gas than in London, as is almost the whole of Scotland. But it is asserted that in the majority of English provincial towns, especially those where the gas works are in the hands of the municipality, the gas is poorer than in London. This charge brought against municipal gas-works is exceedingly improbable, and agrees little with our observations. It is admitted that the tone of the Auer-Welsbach light is unpleasant and greenish.

The heating value of London coal has a power of 155 calories, as against water-gas 72 and Dowson gas 37.

A variety of points connected with lighting-gas, or rather with gas companies, are not touched upon. There is no discussion of the demerits of that "mechanical Ananias," the gas meter. Nor, as we are happy to remark, is their any polemic against the electric light.

Mr. Butterfield, by the production of this book, has laid all concerned under great obligations.

Spiritual Heroes (Guiding Spirits). A collection of Biographies, Edited by D. ANTON BETTELHEIM. Vol. xix., *Darwin, His Life and Activity*, by Professor PREYER, Aulic Counsellor. (Geisteshelden, Herausgegeben von D. Anton Bettelheim. Darwin, sein Leben und Wirken). Berlin: Ernst Hofmann and Co.

THE work before us gives in the brief compass of 208 pages perhaps the most instructive biography of the great reformer of biology which has yet been issued. We notice it with the greater pleasure because its author, Professor Preyer, looks forward hopefully to the extension of the grand principle of evolution to the inorganic world, especially to the chemical elements—referring in this respect to the discourse on the "Genesis of the Elements," delivered by Mr. Crookes in 1887 before the Chemical Section of the British Association—because it throws valuable lights on the origin of genius and on scientific education, and because Darwin, though no chemist, was a careful and successful experimentalist. Had he been placed under slightly different circumstances he might have become an illustrious chemist.

The book opens with a preface by Professor Ernst Haeckel, who speaks of Darwin as "our venerated friend and 'grand master'" ("Altmeister," a term for which we have no exact English equivalent). We come next to an account of Darwin's family, remarkably thorough going and accurate. It is shown to what an extent exceptional intellectual power has prevailed in the family for some generations. The eldest son of Erasmus Darwin (the grandfather of our hero), though he died in his twentieth year from a wound received whilst dissecting, had already given proof of unusual aptitude for the medical sciences. A second son of Erasmus, a genealogist, numismatist, and statistician, died in his 40th year by suicide in an attack of insanity. Francis Galton, a cousin of Charles, is well known for his valuable works on heredity, and Robert Waring Darwin, the father of Charles, was an eminent and successful physician. In short, a study of the career of the Darwin family is a valuable lesson on heredity.

Not less instructive is the next chapter on Darwin's school and university career.

We find that, like Liebig, he was denounced at school as a hopeless dunce, a warning on the folly of estimating youths by their aptitude for the dry stubble of classicism. Neither was he a mathematician, and hence he did not take honours at Cambridge. He derived, however, much benefit from his intimacy with Professor Henslow, who aroused in his mind the latent love for the

study of animal and vegetable nature. He had begun to collect Coleoptera whilst at Edinburgh. The only examination which he "went up for" and passed was that for B.A. at Cambridge, in January, 1831. But in spite of his career at two universities, we may consider him as largely a self-taught thinker and discoverer. He had now escaped several dangers, either of which might have caused him to be lost to science. At Edinburgh he might have become a somewhat dry naturalist, of the school of Professor Jameson. Next, his father wished him to become a clergyman or a physician, but what we must call a fortunate accident intervened. He had the opportunity of joining as naturalist the surveying expedition of the *Beagle* under Captain Fitz Roy. Here he found his true calling, and awoke to systematic and continuous study, and made the observations which ultimately led to his epoch-making work. But for this he had to pay dearly. The *Beagle* was a typical specimen of the ten-gun brigs which then existed in the British navy, and which were notorious for their power of occasioning and intensifying sea-sickness in their crews. From this affliction Darwin suffered all the five years of the expedition, except the short intervals spent on land, and he remained an invalid for the rest of his life. He achieved the wonderful amount of work which he has left us only by the most judicious economy of time and strength.

Professor Preyer's critique of Darwin's theories is of course highly favourable, and is a signal and wholesome contrast to the lamentable comment of M. Blanchard on Lord Salisbury's presidential discourse delivered before the British Association in 1894.

In the account given of the funeral honours paid to Darwin Professor Preyer makes one mistake. The personal attacks on Darwin, and the opposition to the doctrine of evolution, have not ceased, and are indulged in, in France chiefly by the Academy of Sciences, and in England by the "Positivists," whose invectives might, however, be regarded as complimentary.

Exercises in the Preparation of Organic Compounds. By Professor EMIL FISCHER, of Berlin. Translated from the Fourth German Edition by ARCHIBALD KLING, F.I.C. Glasgow: Hodge and Co. London and Edinburgh: Williams and Norgate. 1895. Pp. 80.

It has long been recognised in Germany that as an initiatory training for research the preparation of organic compounds is of the highest value. By such exercises the student learns the arts of manipulation and all the resources necessary for obtaining compounds in the highest state of purity, with the greatest attainable neatness and economy of material and of time, and with the precautions required to avoid dangers. We have here instructions for the preparation of 77 important representative organic substances.

In many instances the characteristic reactions of the product are mentioned as a guide, as also the yield which ought to be obtained. Cuts of the apparatus are given where it has appeared useful. The work has been found exceedingly valuable in the laboratories of several of the German universities, and we hope that Mr. Kling's version will be widely utilised in this country.

An Introduction to the Study of Rocks. British Museum (Natural History), Cromwell Road, London, S.W. Mineral Department. Printed by Order of the Trustees. 1895.

It is to be regretted that the study of mineralogy in the widest sense of the term is far from popular in Britain. Our scientific journals rarely give an account of the discovery or the detailed study of any mineral or rock. This comparative neglect exists in spite of the obvious and

important economic bearings of the question and of the facilities afforded to the student by the collection of the British Museum, even in its present uncentral location. The work before us, which has been drawn up by Mr. L. Fletcher, is enriched with a plan of the mineral gallery at the Museum. The treatment of the subject is clear and simple, and is calculated to be a trustworthy guide to the student. At present we often see, in private collections, a confusion between rocks and mineral species. Some persons who lay claim to no inconsiderable extent of culture deny to a bed of clay or sand the name of a rock or even of a solid. By this error we have known a riparian proprietor who had caused pulverulent matter to be thrown into a stream escape the law concerning the obstruction of streams.

Manual of Metallurgy. (Handbuch der Metallhüttenkunde). By Dr. CARL SCHNABEL, Professor of Metallurgy and Chemical Technology at the Royal Mining Academy of Mines of Clausthal. Vol. I., Copper, Lead, Silver, Gold. With 571 illustrations in the Text. 8vo., pp. 914. Berlin: Julius Springer, 1894.

PROFESSOR SCHNABEL has favoured the technical world with a most elaborate and comprehensive treatise at once theoretical and practical.

Under each metal, *e.g.*, copper, we find a careful account of its physical properties, its chemical attributes, and especially those reactions of the compounds of the metal which are most important for its extraction. Then follows a catalogue of its ores, with their localities, compositions, and percentage of metal.

We then come to its extraction and refining; firstly in the dry way, as applied to copper sulphides, and with different modifications (*e.g.*, pyritic smelting). The author compares the shaft-furnace process, general in Germany and Sweden, with the reverberatory process, common in England, and points out the advantage of the combined process as now in operation both in Germany and England. The Bessemer process for copper may, the author thinks, prove ultimately superior to both.

The various processes are next described in detail with the aid of excellent cuts, for the most part drawn to scale.

The various methods of roasting so as to utilise the sulphurous acid, and to prevent, or at least minimise, the injury produced by its escape into the air, are carefully discussed.

The refining of crude copper is described as performed at Mannfeld, Lake Superior, Pittsburg, Atridaberg, and Oker.

Professor Schnabel then proceeds to the extraction of copper by the wet way, according to the condition in which it occurs.

Concerning the elaboration of copper stones by the electrolytic process, no results have yet been reached which can be pronounced as definitely satisfactory from an economical point of view. With the alloys of copper the results are much more satisfactory.

The metallurgy of lead is next expounded in a similar manner, leading to that of silver. It is to be remarked that the present procedures for the separation of silver from galena fail to give satisfaction, since at the current low prices of silver they are no longer remunerative. Rewards have therefore been offered for some improved method. Electrolysis is here described mainly as applicable to alloys of lead and silver and of zinc and silver. It may, perhaps, not be regarded as an unpardonable digression if we point out that the demonetisation of silver is regarded in some quarters as almost a *casus belli*.

In the section on gold we find that very discrepant statements are made by different authorities concerning its physical properties. Thus its specific gravity is given as 19.30, and again as 20.72. Its conductive power for heat is, according to Despretz, 103 (silver=100), according to

Calvert and Johnson 98, and according Wiedemann and Franz 60.

At present the author considers that, although the cyanide process for the extraction of gold from ores which contain a large proportion of pyrites and ignoble metals is in many cases applicable, yet in the majority of instances the expense of this process is heavier than that of amalgamation or of chlorination. He recognises, however, that the cyanide process is still in its infancy. It may be that the solubility of gold in a mixture of potassium cyanide with ferricyanide is greater than in cyanide alone.

The present volume of Schnabel's treatise will be found most valuable, and the continuation of the work will prove no less satisfactory.

The Chemistry of Chlorophyll. (Die Chemie des Chlorophyll.) By Dr. L. MARCHLEWSKI. 1895. 8vo., Pp. 82. Hamburg and Leipzig: Leopold Voss.

THIS work, which is dedicated to Dr. Edward Schunck, F.R.S., does not profess to be a complete monograph of the substance in question. It does not enter upon the physiology of leaf-green, its origin in the plant, its vital functions, and its relation to other vegetable products. The other confines himself to the chemical phase of chlorophyll as a green compound capable of dyeing green. It is, however, not a unitary colouring matter, but a mixture of two pigments with a fatty acid. Pure chlorophyll, however, *i.e.*, the substance which has been extracted by alcohol from the green parts of plants, has not yet been isolated. The pure so-called crystallised chlorophyll described in chemical literature consists probably of derivatives of true chlorophyll.

Foremost among such derivatives stands chlorophyll as obtained by the action of weak, especially organic, acids upon chlorophyll. By treatment with stronger acids it is transformed into phylloxanthin and phyllocyanin, which have been recently studied by Schunck. Phyllocyanin, again, by treatment with concentrated acids or by alkalies into phyllotaonin, the best characterised derivative of chlorophyll, is one of the most beautiful substances of organic chemistry.

The original unmodified chlorophyll may be transformed by alkalis into alkachlorophyll, which latter compound, on treatment with acids in presence of alcohol, yields an alkylether of phyllotaonin. On heating phyllotaonin with alkalis at a high temperature we obtain phylloporphyrine.

Each of these products is described in full, with the method of its preparation, its properties, its chemical composition, its spectroscopic behaviour, and its fission products.

We heartily share the author's hope that chlorophyll may soon be as thoroughly treated from the physiological point of view. We feel bound to call particular attention to the admirable bibliography which concludes the work and to the two spectroscopic tables.

CORRESPONDENCE.

ON THE PLACE OF HELIUM IN THE CLASSIFICATION OF ELEMENTS.

To the Editor of the Chemical News.

SIR,—The tone of Mr. Wilde's last letter renders it impossible for me to continue the correspondence with him. I would, however, ask any chemists who are interested in the question of priority which he there raises, to look at the papers mentioned in our letters, and judge for themselves.—I am, &c.,

J. H. GLADSTONE.

17, Pembroke Square, W.,
December 31st, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Journal für Praktische Chemie.

New Series, Nos. 5, 6, and 7, 1895.

Researches from the Organic Laboratories of the Technical High School at Dresden.—Communicated by E. v. Meyer.—These researches consist of a paper, by P. W. Uhlmann, on the action of cyanacetic ethyl ester upon the salts of mono-nitro-diazobenzene. The author observes that the behaviour of the aqueous solutions of the potassium salts (1 : 300) was interesting. A stratum 10 m.m. in depth, of the three potassium salts absorbed:—The meta-salt; blue and violet entirely. The para-salt; yellow, green, blue and violet completely, orange partially. The ortho-salt; orange, yellow, green, blue, and violet completely. All the three salts were polarimetrically inactive.

On Complex Metallic Bases.—N. Kurnakow.—First Treatise; Chapter II.; a continuation of Metal Salts of the Thioamides. The metal compounds of the thioamides show us distinctly that, in the formation of a complex salt, both the atoms of the metal and the acid residues are simultaneously concerned. The striking stability of the thio-amido-salts of a higher type lead us to the conclusion that in these substances also several mols. of thiamid are directly combined with the metal.

Researches from the Chemical Institute of the University of Erlangen.—M. Busch.—The present treatise—a continuation—is occupied with a study of orthodibenzylamine. It does not admit of useful abridgment.

A Contribution to the Knowledge of the Homologues of Ethylen-diphenolsulphon and Ethylen-ditolylsulphon, with Communications on the Behaviour of Mercaptides with Halogenalkylenes.—R. Otto.—Not adapted for useful abstraction.

The Occurrence of Orthocumaraldehyd methyl Ether in Cassia Oil.—J. Bertram and R. Kursten.—The authors, working in the laboratory of Schimmel and Co., of Leipzig, whilst rectifying a large quantity of the oil of *Cinnamomum cassia*, obtained a crystalline body probably identical with Rockleder's "cassiastearopton." They identify this body with methylorthocumaraldehyd,—a compound which they have also obtained synthetically.

A New Manner of the Formation of Secondary Aromatic Amines.—O. Kym.—The author states that his results are very fragmentary and incomplete.

Researches from the Laboratory of the University of Freiburg, in Breisgau.—These researches consist of papers on the "History of Bibromsebacinic Acids," by Ad. Claus, and on "Tautomerism" and "De motropy" by the same chemist. He contends that, if we are not disposed to abandon the entire view of the concatenation of atoms, we must extend it to the assumption that even more than two elemental atoms may unite with a corresponding number of valences in one common combination.

Quantitative Determination of Condensation-Products.—G. Vendt.—The author has exemplified his methods in the cases of the condensation of acetanilide to floraniiline by means of zinc chloride, and that of benzene and chloroform by means of aluminium bromide.

On Experiments for the Production of Carbon Monosulphide.—A. Denninger.—The author's experiments have not led to the results desired. He feels justified in assuming that carbon monosulphide is a liquid boiling at a low temperature, and having a pleasant smell of carbon disulphide. It is readily combustible, and is violently absorbed by alcohol and aniline.

Zeitschrift für Anorganische Chemie,
Vol. ix., Part I.

Fluorescent Spectrum of Argon, and its Relations to the Aurora Borealis.—M. Berthelot.—See *CHEMICAL NEWS*, vol. lxxi., p. 212.

A Contribution to the Knowledge of the Copper and Manganese Cyanides.—Paul Straus.—The author describes potassium manganate- and manganic-cyanides, the double decomposition of these salts with ferric and ferrous salts, the potassium cupromangan-cyanides, and the analogous sodium and ammonium compounds, and the potassium cuprocupri-cyanide.

The Double Haloid Compounds of Cæsium, Rubidium, Sodium, and Lithium with Thallium.—J. H. Pratt.—This paper requires the accompanying figures.

The Volatility of Chromic Anhydride.—Henryk Arctowski.—This anhydride is volatile far below its melting-point.

Synthesis of some Ore-minerals and Analogous Metallic Compounds by their Solution and Crystallisation in Fused Metals.—Fried. Rössler.—This memoir requires the accompanying 34 figures.

A Preliminary Communication.—Carl Engels.—With reference to the remark of P. Jannasch, that he is about to undertake the electrolytic separation of metals with the simultaneous presence of organic substances and hydrogen peroxide, the author mentions that he has been engaged for a considerable time with experiments in this direction.

Vol. ix., Parts 2 and 3.

Quantitative Determination of Lead.—A. Kreighauer.—This voluminous memoir requires the accompanying figures. The author's method is electrolytic. It is pointed out that the platinum capsules serving as electrodes should be *turned*, not hammered.

On the Ferrocyanides.—J. Messner.—An examination of Turnbull's blue, of Berlin green, and of Williamson's violet. The individuality of the last-mentioned substance is regarded as questionable.

Experiments for the Production of Pure Zinc.—F. Mylius and O. Fromon.—This paper cannot be reproduced in full without the insertion of the seven accompanying figures. The principal results are that the so-called pure zinc of commerce always contains determinable quantities of cadmium, lead, and iron. Solution of zinc sulphate can be so effectually purified electrolytically that in its chemical analysis we cannot detect any foreign heavy metals. Zinc oxide can easily be obtained chemically in corresponding purity. The electrolytic zinc obtained from zinc sulphate or oxide contains recognisable quantities of platinum derived from the anode. The purest zinc is obtained by repeatedly refining the metal electrolytically in basic solutions of zinc sulphate. The product is spongy, and requires to be re-melted and sublimed *in vacuo*. The metal thus obtained contains at least 99.999 per cent of zinc. In the electrolytic separation of zinc from solutions, the secondary decomposition of water cannot be entirely avoided. The formation of zinc-sponge takes place with the co-operation of oxygen.

The Separation of Metals in a Current of Carbonic Acid charged with Bromine.—P. Jannasch and E. Rose.—The authors describe here the separation of bismuth and cobalt, of bismuth and nickel, of tin and antimony, from lead and copper. The authors' methods cannot be described intelligibly without the three accompanying figures.

Specific Heat of Hydrogen Peroxide.—W. Spreng.—The facts ascertained show accordingly the imperfect consumption in the compound H_2O_2 of the potential chemical energy of the elements H_2 and O_2 . On the other hand, they demonstrate the theorem of De Heen,

according to which the variation of the specific heat of liquids depends on dissociation.

The Action of Ferric Chloride upon Metallic Iodides.—Karl Seubert and Karl Gaab.—A complete abstraction of this memoir would require the insertion of the five tables of curves. In general it may be said that the influence of the metal present as iodide upon the course of the reaction is for the most part insignificant, and always much smaller than that of the acid contained in the ferric salt. In the latter case the presence of sulphuric acid, in place of hydrochloric acid, determines a decrease of the free iodine to the extent of more than 20 per cent of the theoretical quantity. With ferric acetate alone no iodine is liberated.

MISCELLANEOUS.

The Leather Industries.—We are informed that a course of lectures with experimental demonstrations will be given by H. R. Procter, F.I.S., at the Yorkshire College, Leeds, on "Recent Processes in Leather Manufacture." The course will commence on Wednesday, January 15th, 1896. We consider that this course merits the support of all persons connected with the leather trades, not alone from the well-known ability and experience of the lecturer, but because the authorities of the Yorkshire College rightly consider it of the first importance that their lecturers should teach by their own syllabuses and not by those of an extraneous body. By insisting on this principle they deserve the gratitude of all friends of British industry.

On a Possible Procedure for Separating Atmospheric Argon or Nitrogen.—Claudius Linb.—One of the best procedures for separating argon from atmospheric nitrogen consists in absorbing the latter by means of lithium. Unfortunately this metal is very rare, and the lithium thus obtained has consequently an excessive price. I have indicated that simple barium fluoride or barium and sodium double fluoride treated with sodium at a moderate heat yield a grey substance, evidently reduced barium, which absorbs the nitrogen of the air energetically. It would be easy to make this preparation in a stout iron tube, which would then serve for the passage of atmospheric air, previously deprived of its watery vapour, its carbonic acid, and its oxygen. The price of sodium and of the fluoride, double or single, prepared as I have indicated, being low, we might have argon relatively cheap. The procedure, always supposes that argon resists this absorbent; if the contrary is the case the fact will still be interesting. I purpose to experiment on this process and determine with precision the physical and chemical properties of this gas.—*Comptes Rendus*, cxxi., p. 887.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Medical, 8.30.

TUESDAY, 14th.—Institute of Civil Engineers, 8.

— Photographic, 8.

— Royal Medical and Chirurgical, 8.30.

— Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.O.S.

WEDNESDAY, 15th.—Society of Arts, 8.

— Meteorological, 8. (Anniversary).

— Microscopical, 8. (Anniversary).

THURSDAY, 16th.—Royal Institution, 3. "Dante," by Philip H. Wicksteed, M.A.

— Royal, 4.30.

— Royal Society Club, 6.30.

— Institute of Electrical Engineers, 6.30.

— Chemical, 8. "The Acetylene Theory of the Luminosity of Hydrocarbon Flames," by Prof. Vivian B. Lewes. And other papers.

FRIDAY, 17th.—Quekett Club, 8.

— Royal Institution, 3. "More about Argon," by The Right Hon. Lord Rayleigh, F.R.S.

SATURDAY, 18th.—Royal Institution, 3. "To the North of Lake Rudolf and among the Gallas," by Dr. A. Donaldson Smith, F.R.G.S.

THE CHEMICAL NEWS.

VOL. LXXIII., No. 1886.

NOTE ON THE RAPID ESTIMATION OF INSOLUBLE PHOSPHATE.

By VINCENT EDWARDS, F.C.S.

THERE can be no doubt that the estimation of both "soluble" and "insoluble" phosphates in manures is best effected by weight, but at times, when results are required without delay, the volumetric method by means of uranium acetate is extremely useful, and with precautions good results can be obtained, especially with superphosphates and dissolved guanos. This applies, however, more to the "soluble" determination than the "insoluble." In the latter case various substances become dissolved and render the end-reaction with ferrocyanide obscure, and the results therefore untrustworthy. Though I would certainly not advocate the substitution of any volumetric process for the usual gravimetric one, I made a few experiments to ascertain, as a matter of interest, the most suitable conditions under which the "insoluble" phosphate in manures can be estimated by titration with solution of uranium acetate, and venture to submit as the most satisfactory the following:—

I take a small quantity of the well mixed sample, about 0.5 grm., and exhaust with cold and hot water, collect the undissolved matter as usual on a small Swedish filter-paper, and washing till the filtrate coming through is no longer acid. The residue is then washed off the filter-paper with hot water into a small beaker, and treated with a very small quantity of HCl and boiled on a sand-bath for a short time. The hot solution is then run through the same filter into a larger beaker, the sand washed, and the filtrate diluted to 300 c.c., ammonia added till alkaline, and afterwards acetic acid till just acid. The smaller the amount of HCINH_3HO and $\text{HC}_2\text{H}_3\text{O}_2$ employed the better. The beaker is then placed on a sand-bath, heated till warm, and a few drops of uranium acetate run in, and the heating continued till the usual precipitate appears; the titration is then carefully finished, a deep colour being taken as the end-mark. The results by this method may be a trifle low, but with care will be found very near those by weight. The dilution greatly increases the accuracy of the method, and it is possible that a weaker solution of uranium might be also used with advantage for the "insolubles" than the ordinary one (1 c.c. = 0.01 grm. $\text{Ca}_3\text{P}_2\text{O}_8$), and I intend to try some experiments on this point.

Work's chemists, who are often called on to furnish rapid results for home use, will do well to try this plan. I need scarcely say the uranium must be standardised under the same conditions as the titrations are made.

Lawes' Works, Barking, Essex,
January 1, 1896.

THE CHLORIDES OF ZIRCONIUM.

By F. P. VENABLES.

In a report upon the examination of the chlorides of zirconium (*Journ. Amer. Chem. Soc.*, 1894, xvi., 460-475) it was stated that pure zirconium tetrachloride was formed by the solution of zirconium hydroxide in hydrochloric acid and repeated crystallisation from the concentrated acid. This statement was based on a partial analysis by Linnemann (*CHEMICAL NEWS*, lii., 233-240), the result of which made him call the substance the

tetrachloride; and on repeated partial analyses of my own, in which the zirconium present was determined by ignition as zirconium dioxide. So firmly convinced was I of the fact that this was the normal tetrachloride that I determined to use it in revising the atomic weight. Ten closely agreeing determinations were made, and they yielded, as the percentage of zirconium dioxide found, 52.99, or, calculating with 90.62 as atomic weight of zirconium (Bailey), 39.16 per cent of zirconium. The zirconium in the tetrachloride amounts to 38.99 per cent.

Bailey made several very widely differing determinations of the chlorine in this body, and considered it the oxychloride. His determinations varied so greatly, and his mode of drying was so faulty, that I simply concluded he was mistaken, being unable to detect a source of error in my analyses which would allow for a change from 39.16 per cent of zirconium to 46.79 per cent, the amount needed for the oxychloride.

Still, as a necessary precaution, I made some determinations of the chlorine in the pure crystalline product, and was greatly surprised to find only 35.5 per cent of chlorine instead of 61.01, the amount required for the tetrachloride. The percentage in the oxychloride would be 36.63.

I regard the results as very singular. The substance must be an oxychloride, but what is its composition? The simplicity of its preparation, and the constancy of its composition along with its stability, would argue for a simple formula. No such formula can be calculated from the analysis. Probably the best formula suggested for this oxychloride, corresponding closely with the above analysis, is $\text{Zr}_3(\text{OH})_5\text{Cl}_7\cdot 5\text{H}_2\text{O}$. — *Journ. Amer. Chem. Soc.*, vol. xvii., p. 842.

ON THE ANALYSIS OF ALLOYS OF LEAD, TIN, ANTIMONY, AND ARSENIC.

By LAUNCELOT ANDREWS.

The experiments described in the present paper were carried out under my direction, during the last winter, by Mr. Earl Durfee. Part of them were suggested by Drown's investigation of the separation of tin from lead by repeated evaporations with concentrated hydrochloric acid, but were carried out previous to the publications of Jannasch (*Ber. d. Chem. Ges.*, xxvii., 3335), and of Jannasch and Schmitt (*Zeitsch. Anal. Chem.*, ix., 274) on the same subject. All experiments referred to here relate to the analysis of an alloy containing in round numbers 80 per cent lead, 13 per cent antimony, 7 per cent tin. The exact composition of this metal will be given later.

First Method.

The attempt was made to drive off all tin and antimony as chlorides, according to Drown. To this end 1 grm. of the alloy was dissolved in aqua regia and evaporated to dryness, heating the residue to 200° C. The latter was moistened with about 4 c.c. fuming hydrochloric acid, and evaporated as before, the whole operation being repeated five times. The remaining lead chloride was, however, not free from tin and antimony. A series of attempts were then made to effect a separation by treating the alloy with bromine and hydrochloric acid gas, in varying forms of apparatus and at various temperatures. The details of these experiments need not be given, since they either failed to give a complete separation or were affected by practical faults of one kind or another.

On the other hand, no difficulty was found in completely volatilising all the tin and antimony by heating the alloy directly, without previous solution, in a current of hydrochloric acid gas which had passed through concentrated nitric acid. The process was carried out as

follows:—Hydrochloric acid gas, evolved in a slow and steady stream by allowing the fuming acid to flow through a capillary tube into concentrated sulphuric acid, passes first through a flask containing 10 c.c. of nitric acid of 1.50 sp. gr., and then through a combustion-tube of large diameter, 30 c.m. long, containing a porcelain boat with the alloy in the form of turnings. The current of gas on leaving the combustion-tube traverses a Volhard absorption flask, charged with a solution of potassium bromide and kept cold during the process. The combustion-tube is covered with an asbestos tent, and heated, by means of an Argand burner, to 210° C. The amount of the alloy used in each experiment was a half grm., and in two hours—during which time the operation required no attention whatever—the separation was complete, and the snow-white residue in the boat was completely soluble in boiling water, while the distillate in the receiver was free from lead. The lead was weighed as sulphate. The receiver contained the antimony and tin and a little arsenic. To it was added the solution obtained by rinsing the unheated part of the combustion-tube with hydrochloric acid. The small amount of arsenic present was easily separated from the contents of the receiver by distillation according to Gooch and Phelps (*Zeitsch. Anal. Chem.*, vii., 123). After the removal of the arsenic, tin and antimony were separated by Carnot's method (*Zeits. Anal. Chem.*, lxxxviii., 650), which was found to be excellent.*

The process as described may be modified by attacking the alloy with nitric acid first, in a two-necked flask, then evaporating in a current of hydrochloric acid gas and heating in the same as before. The quantitative results are concordant, but the modified process is less convenient and requires decidedly more time.

Analytical Results.

	I. Grm.	II. Grm.	III. Per cent.	IV. Per cent.
Alloy taken	0.5000	0.5000	—	—
Lead sulphate	0.5849	0.5853	—	—
Lead found	0.3988	0.3991	79.75	79.82
Antimony trisulphide..	0.0925	0.0925	—	—
Antimony found.. ..	0.0661	0.0661	13.21	13.21
Stannic oxide	0.0434	0.0437	—	—
Tin found	0.0342	0.0344	6.84	6.88
Arsenic (volumetrically)	0.0006	0.0007	0.12	0.14
Total			99.92	100.05

Second Method.

It has been observed that, when various kinds of anti-friction metal or type metal were boiled with hydrobromic acid or with mixtures of hydrochloric acid and potassium bromide, the antimony remained undissolved, the arsenic distilled off, and all the other constituents of the alloy went into solution. A more critical examination of the matter showed that, under the conditions named, in the presence of air, a small amount of the antimony dissolved, but that the undissolved portion was free from lead and tin. On the theory that the partial solution of the antimony was due to the oxidising action of the air, it seemed likely that the addition of a powerful reducing agent, such as hydriodic acid, would prevent the loss of antimony, a view which was confirmed by an experiment in which potassium iodide took the place of the bromide.

One grm. of the metal, in turnings, after boiling for one hour with hydrochloric acid of 1.10 sp. gr. and potassium iodide (about 1 grm.) was entirely disintegrated. The antimony remained undissolved as a dark grey powder. It was filtered from the boiling solution through a Gooch

filter, washed with boiling water until free from lead iodide, dried, mixed with sulphur, and gently ignited in a stream of carbon dioxide. This conversion into sulphide is needful because the finely divided antimony obstinately retains either water or hydrogen, in consequence of which the results come about seven-tenths per cent too high if the metal is weighed directly.

Analytical Results.

	I.	II.
Metal taken	1.0000	1.0000 grm.
Antimony weighed direct	0.1385	0.1375
Antimony trisulphide ..	0.1827	0.1833
Antimony calculated ..	0.1305	0.1310
Antimony.. ..	13.05	13.10 per cent.

The subjoined table presents a summary of the results obtained by the different methods of analysis of the same alloy. Column I. gives the results obtained by tedious but exact methods, not described in this paper but employed for a control. Column II. gives the figures obtained by the first method above described. Column III. those of the second method. Column IV. the mean of all of the results.

Summary.

	I. Per cent.	II. Per cent.	III. Per cent.	Mean. Per cent.
Arsenic..	0.13-0.12	0.12	0.14-0.13	0.128
Antimony	13.13-13.15	13.21-13.21	13.05-13.10	13.14
Tin ..	6.83-6.84	6.84-6.88	—	6.85
Lead ..	79.87-79.95	79.75-79.82	—	79.85
Total				99.97

In conclusion, I wish to draw attention to a convenient device for maintaining temperatures lying between 200° and 500°, which are difficult to secure with certainty by means of a Bunsen, or even in some cases by the ordinary forms of air-bath. The device consists simply of an ordinary Argand gas-burner with chimney, as made for illuminating purposes, with the addition of a simple hood or tent of asbestos and sheet-iron to go over the top of the chimney and confine the heat. It is surprising what a wide range of temperatures this simple apparatus gives command of. It is very perfectly adapted for the ignition of antimonous sulphide in carbon dioxide, an operation which can be carried out with great nicety at 400°, but which is difficult and uncertain when a Bunsen burner is used as the source of heat. Many other operations, distillations, digestions, &c., are carried on advantageously in this way, the great merit of the arrangement consisting in the superior control of the temperature. It is, for example, well adapted to the conversion of calcium oxalate into carbonate. — *Journ. Amer. Chem. Soc.*, vol. xvii., p. 869.

ON THE CONSTITUTION OF WATER AND THE CAUSE OF ITS DISSOCIATIVE POWER.

By J. W. BRÜHL.

In the aqueous solutions of salts of strong acids and bases the observed alteration of the freezing- and boiling-points is known to be approximately twice as great as it ought to be normally, and according to the original equation of van't Hoff. We know, likewise, that this apparent abnormality has been removed by Arrhenius, who showed that all substances which behave in this manner in aqueous solutions are electrolytes, the dissociation of which into ions must have the above behaviour as a consequence.

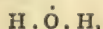
It is, further, known that many kinds of organic bodies in certain solvents form double molecules or larger mole

* In this method the solution, containing an oxalate and free oxalic acid and much ammonium chloride, is boiled with sodium thiosulphate. Beside the precautions given by the originator of the method, it is essential to success that the solution be boiled violently until one-fourth is boiled away, and that, finally, the acid be in excess as regards thiosulphate.

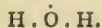
cular complexes. This is especially the behaviour of the fatty acids, the oximes, the alcohols, &c., when dissolved in hydrocarbons, in chloroform, or in carbon disulphide. On the other hand, the complex molecules are broken up when such bodies are dissolved in water. Alcohols, ethers, esters, ketones, phenols act likewise as dissociative media, though less completely. These latter organic solvents prove also to a certain degree ionising agents, as, e.g., it appears that when saturated with hydrochloric acid gas they have a greater or less conductivity, whilst solutions of hydrochloric acid in benzene or other hydrocarbons have little or no conductive power.

It is not yet sufficiently explained how the dissociating action of the above-named solvents arises, and especially why, in this respect, water by far surpasses all known substances.

The tetravalence of oxygen was rendered probable by Ch. Friedel twenty years ago, and has been confirmed by the author's researches on hydrogen peroxide. If hydrogen peroxide has the constitution $H.O : O.H$, the formula of water must be—



i.e., it must be regarded as a non-saturated compound. In fact, of all known substances, none displays the criteria of non-saturation in so striking a degree as water. Nearly all bodies have the tendency to combine with it, i.e., they are hygroscopic; there exist numberless hydrates and compounds with crystalline water; and, finally, water is the most universal solvent. All this argues unanimously for the presence of unexhausted affinities, which is satisfactorily explained by the formula



The supplementary valences of the tetravalent oxygen are evidently the cause of the power of splitting off ions, and of the dissociative power of water which is brought into play, as against molecular aggregates. These same supplementary valences are the focus of the creative power by means of which water plays so weighty a part in the household of nature.

This theorem receives further and very essential support in the fact that all those organic solvents which are known as good dissociating media, i.e., the alcohols, ethers, esters, ketones, phenols, urethan, &c., contain oxygen, whilst the non-dissociative or feebly dissociative media, such as the hydrocarbons, carbon disulphide, chloroform, carbon chloride, are all free from oxygen. Further, the substances especially capable of association, such as the carbon acids, the alcohols, and oximes, are oxygen compounds, and that water, in particular, forms complex molecular aggregations.

From all these considerations we may regard it as established that it is the presence of water, principally if not exclusively, which determines the tendency of the above-mentioned substances to form complex molecules, and also occasions the dissociating force. Water has the greatest proportion of oxygen and the greatest dissociative power; then follows in this respect, among the alcohols, in the first place, methylic alcohol, whilst its higher homologues decrease more and more in capacity for association and in dissociative power. The competition for the atom of oxygen becomes the stronger the more other kinds of atoms are present in a molecule, and the more completely its tendency to combination is satisfied.

Hydrogen peroxide is very much richer in oxygen than is water. In this substance, that tendency of the hydrogen atoms to combination is gratified only to a small extent. Further, the so-called triple bands of the molecule, $H-O \equiv O-H$, may be resolved, and hence hydrogen peroxide may be regarded as a highly non-saturated body—to a greater extent than water. The conjecture is forced upon us that hydrogen peroxide must possess a great dissociative power, probably still greater than that of

water. This cannot be readily shown in a direct manner by the electrolysis of dissolved bodies, or by cryoscopic and ebullioscopic determinations, on account of the instability of hydrogen peroxide. But it will be possible in an indirect manner.—*Comptes Rendus*, cxxi, p. 2866.

THREE NEW REAGENTS FOR NITRITES.

By G. DENIGÈS.

AMONG Griess's reagents, which are being more and more used for the detection of nitrous acid, the salts of meta-phenylenediamine are especially admired. Along with their excellent properties, they possess various defects, e.g., they are attacked by the halogens, by hypochlorites, and hypobromites, and their solutions are readily decomposed by air. The author recommends the following reagents which are, in part at least, free from these defects:—

1. Phenol, if boiled with Millon's reagent, gives a precipitate which dissolves in acetic acid with a red colour. This reaction renders it possible to detect phenol at a dilution of 1 : 2,000,000. Millon's reagent is a solution of mercury nitrite and nitrate; the effective substance being the mercurous nitrite or nitrous acid in presence of a mercurous salt. Hence, for the detection of nitrous acid the author uses the following solutions:—(a) Phenol, 1 gm.; sulphurous acid, 4 c.c.; water, 100 c.c. (b) Mercuric oxide, 3.5 grms.; glacial acetic acid, 20 c.c. water are mixed; $\frac{1}{2}$ c.c. of sulphuric acid is added, and the mixture is filtered. For use, equal volumes of a and b are mixed, heated to ebullition, when 1 or 2 drops of the solution in question are added. If 0.5 gm. nitrite is present in 1 litre of liquid a red colouration appears.

2. 2 c.c. aniline are dissolved in 40 c.c. glacial acetic acid and made up with water to 100 c.c. Of this solution, 5 c.c. are boiled with a corresponding quantity of the liquid in question. (In very concentrated solutions 1 drop is sufficient). In presence of nitrous acid there appears a straw-yellow or a deep orange-colour, which on cautious acidulation passes into a red. Chlorates and nitrates do not interfere as do hypochlorites, hypobromites, free chlorine, and bromine. An excess of acid may interfere, whence strongly acid liquids should be previously neutralised.

3. Resorcin, 1 gm.; water, 100 grms.; sulphuric acid, 10 drops. Place in a test-tube 10 drops of the liquid to be tested, 2 c.c. of pure sulphuric acid, 5 drops solution of resorcin, and shake up. The presence of nitrous acid produces a carmine-red or violet-blue solution, which is very intense at 0.01 m.grm.—*Journal de Pharmacie et Chemiker Zeitung*.

THE TOXICOLOGICAL DETECTION OF AQUA REGIA.

By P. MOLA.

THE author has established by experiments on meat mixed with aqua regia (100 grms. meat, 500 grms. water, and 2 c.c. aqua regia) that, at common temperatures, the mixture does not evolve the slightest traces of chlorine or hydrochloric acid, but traces of nitrous acid. If such a mixture is submitted to fractional distillation, raising the temperature gradually to 140° and 170°, we always obtain neutral distillates, and a faint acid reaction is obtained only on raising the temperature to 190°. In these distillates traces of nitrous acid may be recognised, but not of nitric or hydrochloric acid. The residual substance has a strongly acid reaction, depending on the formation of acid albumens. Distillation is therefore useless for the detection of aqua regia in organic matter. The best pro-

cess is that proposed by Vitali for the detection of hydrochloric acid. The substance in question is heated in a porcelain dish to 50–60°, and gradually mixed with small portions of finely pulverised quinidine until the acid reaction has disappeared. The liquid portion in which the two acids are present as quinidine hydrochlorate or nitrate is filtered off; the filtrate is concentrated and mixed in a large glass tube with two-thirds of its volume of chloroform. To this mixture alcohol is added sufficient to dissolve the chloroform, which is then again eliminated by the addition of water. Both the quinidine salts remain dissolved in the chloroform, the solution is filtered through a double filter, the chloroform is evaporated off, and the residue is taken up in hot water. In this solution nitric and hydrochloric acids can both be detected by their reactions.—*Boll. Chim. Farmac. and Chemiker Zeitung.*

ON THE COLOUR OF THE IONS AS A FUNCTION OF THE ATOMIC WEIGHTS.

By JULIUS THOMSEN.

THE *Zeitschrift für Anorganische Chemie*, vol. x., p. 153, contains a treatise by Carey Lea "On the Relation of the Colours of Atom, Ion, and Molecule."

In it the author arrives at the conclusion that the received periodic system appears non-acceptable as being built upon erroneous principles, and proposes in its stead another form, founded upon the colour of the ions. But the dependence of the colour of the ions upon the atomic weight appears quite simple if we use the form of the periodic system which I have published (*Zeit. Anorg. Chemie*, ix., p. 192). The dependence can then be simply expressed by the following words:—"Only the ions of the mean numbers of the greater series are coloured." The two first series, each with seven members, contain no coloured ions; the two next, with seventeen members each, contain in each series seven to eight coloured ions from titanium to copper, and from niobium to silver; and in the fifth series, with thirty-one members, some of which are as yet undiscovered, we also find in its middle the groups of coloured ions (from cerium to gold); whilst in all the series colourless ions correspond to the extreme members.—*Zeit. für Anorganische Chemie*, x., p. 153.

CONTRIBUTIONS TO THE SEPARATION OF MERCURY FROM THE METALS OF THE ARSENIC AND COPPER GROUP.*

By CARL VON USLAR.

POLSTORFF and Bülow have shown that mercury can be very sharply and conveniently separated from lead, silver, bismuth, and copper, as also from arsenic and antimony, by treating their sulphides with a mixed solution of potassium sulphide and hydroxide.

The sulphides of the four former methods are then left entirely undissolved, whilst mercury sulphide passes into solution along with arsenic and antimony sulphides. From this solution mercury sulphide can be separated quantitatively by the addition of ammonium chloride, whilst arsenic and antimony remain entirely in solution.

This method is found useless for the separation of mercury and from tin. In presence of cadmium sulphide mercury sulphide is very imperfectly dissolved by the mixture of potassium sulphide and hydroxide, and from the solution of tin disulphide and mercury sulphide in the above mixture tin sulphide is always separated along with

mercury sulphide in considerable quantity on treatment with ammonium chloride, whilst at the same time a part of the mercury sulphide remains in solution along with the rest of the tin sulphide.

Polstorff has attempted to separate mercury from the metals of the copper and arsenic group by H. Rose's method, i.e., by separation as mercurous chloride by means of phosphorous acid.

Rose has shown that mercury can be quantitatively separated from single metals of this group by means of phosphorous acid, in presence of all the metals in question. Polstorff has hitherto found the separation impracticable.

In my experiments here described I have used the same metallic compounds employed by Bülow, prepared and tested as described in his dissertation. But I preferred using pure copper oxide in place of copper sulphate.

For the separation of mercury I used a phosphorous acid obtained in the known manner by the deliquescence of phosphorus exposed to the air.

The phosphorous acid thus obtained certainly contains some arsenious acid, but, as direct experiments, show so little that the presence of this impurity occasions no inconvenience even in the separation of mercury from arsenic and antimony.

In order the better to measure off the phosphorous acid for the several experiments, the syrupy acid was diluted with four parts of water by weight. Of this syrup—at about 20 per cent—about 5 c.c. were used to 0.1 gm. of mercury chloride. The separation of the mercurous chloride was effected at a temperature of about 40°. It did not seem advisable to separate the mercury at the ordinary temperature, since it would then be necessary for the mixture to stand for ten to twelve hours, and on prolonged standing in the cold, as also in the presence of free mineral acids, there easily ensues a separation of phosphites or phosphates of the metals of the copper group. The separations were effected simultaneously in hydrochloric and nitric solutions in order to decide whether the presence of either of these acids is more favourable to the separation than that of the other.

The separations in hydrochloric solution were carried out in duplicate, in one with a smaller, and in the other with a larger addition of hydrochloric acid, and in all the separations about equal quantities of liquid (150 c.c.) were used. The mercurous chloride was not directly weighed as such, since in its separation in heat a further reduction to metal readily takes place. It was found this reduction to metal ensues especially readily in presence of much hydrochloric acid, whilst it was not observed in nitric solutions. It appeared also desirable to test the mercurous chloride liberated as to its purity, i.e., to determine whether it is quite free from compounds of the other metal from which it had to be separated. This examination in the case of all metals except cadmium and tin can be effected readily and without loss by the method elaborated by Polstorff and Bülow.

In order to escape needless repetitions in describing the various separations, I will here describe the procedure adopted.

The solution of the metallic compounds mixed with the quantities of acid stated in the several experiments was diluted to 150 c.c. heated to 40–45°, and the phosphorous acid was then added. It was then allowed to stand at the most uniform temperature from five to six hours, with frequent stirring. The precipitate was then collected and thoroughly washed with highly diluted hydrochloric acid or nitric acid. The filtrate was mixed as a check with a few c.c. of the solution of phosphorous acid and allowed to stand for some hours at a temperature of about 40°. If a further separation took place it was collected, well washed, and added to the former precipitate. From the filtrate the metal was separated in a suitable manner as indicated in the several experiments, and weighed. The filter, or otherwise the two filters, with the precipitate of mercurous chloride was placed in a beaker mixed with

* *Zeitschrift für Analytische Chemie*, vol. xxxiv., p. 391.

potassium chlorate (0.5 gm.) and hydrochloric acid (25 per cent), allowed to stand in the cold for some hours, and was then heated on the water-bath with a little water until the odour of chlorine had completely disappeared. It was then filtered, the residues of the filter were washed with hot water containing hydrochloric acid, and the filtrate was heated on the water-bath and precipitated with hydrogen sulphide. The precipitate was collected, rinsed back from the perforated filter into the beaker with hot water containing potassium sulphide, and digested with the mixed solution of potassium sulphide and potassium hydroxide. If there remained a slight residue—which was the case only in the separation of mercury from bismuth and lead—it was collected and united to the bulk of the metal in question. From the solution the mercury was separated as a sulphide by heating with ammoniac, the sulphide was again dissolved in hydrochloric acid and potassium chlorate, the solution perfectly free from chlorine was precipitated with hydrogen sulphide, observing the conditions specified by Polstorff and Bülow, the mercury sulphide collected on a weighed filter, and dried until the weight remained constant. After weighing I convinced myself each time of the purity of the mercury sulphide by incinerating the filter and precipitate in a weighed porcelain crucible.

My researches had in the first place the purpose of ascertaining a method which should permit us to separate mercury from the metals of the arsenic and copper group, if all the frequently occurring metals of this group are present. But as the salts of several metals of this group are soluble in water without decomposition only in presence of considerable quantities of free acid, it was necessary to use rather strong acid solutions for such separations. There were hitherto no accounts of the influence of considerable quantities of free acids on the precipitation of mercury as chloride by phosphorous acid.

H. Rose merely states that in precipitating mercurous chloride it is necessary to operate in an acid solution, but he does not give the quantities of acid which must be added for the precipitations. In the text-books of quantitative analysis, by Fresenius and Finkener, we find it merely laid down that a strong dilution is necessary in presence of nitric acid. It seemed hence important to determine whether the precipitation of mercurous chloride by Rose's method is affected by the presence of considerable quantities of hydrochloric or nitric acid. To this end the following experiments were performed.

(a) Taken, 15 c.c. hydrochloric acid and the same weight of phosphorous acid. The liquid was allowed to stand for four hours at a temperature of 40°. The mercurous chloride was entirely precipitated, but its grey colour indicated a partial reduction to the state of metal.

(b) Taken, 20 c.c. nitric acid (of 25 per cent). The mercurous chloride was snow-white, so that no reduction to metal was recognised.

In both experiments the method above described was adopted and the mercury was determined as sulphide.

Here, as in subsequent separations, it was manifest that a reduction to the state of metal does not ensue in a nitric solution, whilst in hydrochloric solutions the reduction frequently goes on to the metallic state, especially if the quantity of acid is large. Hence the separations, if at all possible, should be effected in a nitric solution, as in case of a reduction to metal volatilisation is very possible.

Separation of Mercury from Copper.

In all experiments the copper was weighed out as oxide. In order to obtain pure copper oxide, a hot solution of perfectly pure copper sulphate was poured in an excess of a boiling solution of soda in a large platinum capsule. The precipitate was washed in the platinum capsule until the sulphuric acid reaction disappeared, dried, and slightly ignited. The precipitate was then heated for some time in the capsule with solution of soda, in order to decompose any possible traces of basic sulphate; thoroughly washed, dried, and slightly heated.

The cupric oxide was now found quite pure, and its purity was then analytically demonstrated.

Before proceeding to separate the mercury from the copper, I satisfied myself, by qualitative experiments, that phosphorous acid on being allowed to act for eight hours at the temperature of 40° occasioned no separation of copper phosphate or phosphite. The experiments proved that the separation of mercury from copper can be effected smoothly by means of phosphorous acid in presence of either hydrochloric or nitric acid.

Separation of Mercury from Cadmium.

The cadmium was weighed as oxide. Before weighing the cadmium oxide was ignited and then allowed to cool in the exsiccator. The separation was effected both in hydrochloric and in nitric solutions.

In the separation of mercury from cadmium, an examination of the separated mercurous chloride for the presence of occluded cadmium compounds, according to the potassium-sulphide-hydroxide method, was excluded, since, as the experiments of Bülow have shown, this method does not admit of a smooth separation of the two metals.

Hence the mercurous chloride was converted into mercuric chloride by digestion with hydrochloric acid and potassium chlorate, and the solution of the latter after the free chlorine had been completely expelled by heat, was directly precipitated with hydrogen sulphide. On subsequently testing the weighed precipitate of mercury sulphide, it was found completely volatile, and therefore contained no admixture of cadmium.

The re examination of the filtrates with phosphorous acid proved that a digestion for five hours is sufficient for the complete elimination of the mercurous chloride. The presence of an excess of hydrochloric acid (about 5 per cent) occasioned a partial reduction of the mercurous chloride to the state of metal. If nitric acid is used the precipitate is snow-white.

In the filtrate from the mercurous chloride, the cadmium is thrown down as sulphide; the sulphide is dissolved in hydrochloric acid with the addition of a small quantity of potassium chlorate. From the solution the cadmium is precipitated as a carbonate at a boiling temperature by sodium carbonate, avoiding excess. The liquid is then kept for some time in ebullition, filtered whilst still boiling, washed with boiling water, the precipitate is dried, and the dried precipitate after being separated as completely as possible from the filter is placed upon glazed paper. The remnants of the precipitate still adhering to the filter are dissolved in hot dilute nitric acid, the solution is evaporated to dryness in a weighed porcelain crucible on the water-bath, and gently ignited. When cold, the bulk of the precipitate is added to the residue and heated, at first gently and then strongly, until the weight is constant.

(To be continued).

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 17.)

CHAPTER IV.

CHEMICAL RESEARCHES ON CARBONATE, SULPHATE, AND CHLORIDE OF LITHIUM.

WHEN undertaking my researches on lithium, my principal object was to ascertain whether the carbonate of this metal, prepared in different manners, could be reduced to a state always identical with itself. These researches have enabled me to show that the method pointed out by M. L. Troost, which consists in dissolving the carbonate

of lithium in water containing carbonic acid, to eliminate the greater part of the sodium, attains that end most rapidly; and that the use of sesqui-carbonate of ammonium, to precipitate this compound of lithium, is the only one to be recommended. I learnt, moreover, that the precipitation of the salts of lithium by carbonate of ammonium ought to be performed in platinum vessels. If it is done in glass, as I used to do it *unwittingly*, silica, lime, and sodium are introduced from the glass. Glass is rapidly attacked by sesqui-carbonate of ammonium. I have found that a Bohemian glass beaker lost 0.023 grm. in weight during the time necessary to raise half a litre of very slightly ammoniated water from 15° to 100°, and that, in this case, it added 0.011 grm. of silica to the ferric hydrate made in this ammoniated water.*

These researches demonstrate that oxalate of ammonium does not entirely precipitate the calcium contained in a concentrated solution of nitrate of lithium, and also that sulphate of ammonium is not able to eliminate a salt or hydrate of barium in solution, from this nitrate.

Lastly,—a less-known fact,—absolute alcohol, when mixed with twice its volume of ether, dissolves in salts of barium, remaining in either melted or dissolved nitrate of lithium, owing to the presence of sulphate of ammonium.

Having mentioned these facts, I must describe the preparation of carbonate of lithium, which was done on two different occasions by M. Rommelaere, working each time on 500 grms. of commercial carbonate of lithium.

I will first describe the method as it was originally followed, and I will then point out the modifications I thought necessary to introduce into it.

The carbonate, suspended in five times its weight of water, was dissolved in nitric acid in such a way as to obtain a solution of nitrate and carbonate of lithium. The solution, contained in a large flask with a ground-glass stopper, was saturated with sulphuric acid, and left in it for twenty-four hours. After it had become clear and colourless, it was filtered and collected in another large flask, and the clear liquid was kept boiling for some time, to eliminate the carbonates of lithium and magnesium. The nitrate solution, having settled and having been filtered, received successively an excess of pure oxalate of ammonium to precipitate the calcium, and, having settled and having been re-filtered, an excess of baryta water to eliminate the final traces of magnesium; finally, after having settled and been filtered once more, an excess of sulphate of ammonium, to precipitate the barium.

As the liquid holding the sulphate of barium in suspension did not pass clear through a double filter-paper, notwithstanding it had been boiled, it was left to settle naturally, which took a very long time. Having become clear, it was decanted, filtered, and evaporated to dryness in a porcelain dish; the nitrate was melted and poured into a platinum dish. The colourless mass with an alkaline reaction was immediately powdered, put into a flask with a ground-glass stopper, and taken up by the least possible quantity of absolute alcohol necessary to dissolve the nitrate of lithium. To this solution was added some anhydrous ether until a small part of the lithium salt was precipitated; it was then left to settle naturally. This having happened, the flask was put in a freezing mixture of sea-salt and ice. The liquid in it was slightly clouded, and the flask was kept at a low temperature until the liquid was quite clear; it was carefully decanted, fil-

tered, and evaporated to dryness in a glass flask. The nitrate was taken up by the least possible amount of water, and the solution was precipitated by an excess of concentrated ammonia, saturated with sesquicarbonate of ammonium.

The flask was heated on a water-bath until ammonia gas was freely given off. When the carbonate of lithium, from being gelatinous, had become granular, it was poured into a funnel furnished with a clean linen plug. The elimination of the filtrate, and washing with water containing bicarbonate of ammonium, and then with pure water, were done with the filter-pump.

The carbonate of lithium was taken up by nitric acid; and the nitrate solution, which was quite clear, was precipitated a second time by sesqui-carbonate of ammonium. The separation of the filtrate and washing with carbonate of lithium were effected as described above. Lastly, all these operations were repeated a third time.

This carbonate of lithium, in a Bunsen flame, showed a comparatively strong sodium spectrum as well as the red lithium line, *but no other line*.

As a check, I volatilised an appreciable quantity of the same carbonate in an *oxyhydrogen* blowpipe, on a platinum sheet.

When the *greater part* of the lithium was evaporated, and the temperature was raised to the fusing-point of platinum, the red and green lines of the calcium and barium spectra were visible, in addition to the three lithium lines.

This experiment was tried several times, and always with the same result. There is no doubt the solution of nitrate of lithium in *etherised absolute alcohol*, made as I have just described, contained, besides sodium, barium and calcium.

It was heated, so as to completely volatilise the oxides of lithium, barium, and calcium, and there remained a *very slight* residue of silicate of barium and calcium, fusible but refractory, covering the platinum surface—which had been tarnished by oxide of lithium—with a thin white glaze.

A fresh preparation, most carefully made by M. Rommelaere in the same manner, gave exactly the same results.

The method I discovered, twenty-five years ago, of procuring carbonate of lithium, only purified it by reason of the successive re-solutions I made, in water saturated with carbonic acid, to get rid of the sodium. The barium and calcium were left in the undissolved portion of the carbonate of lithium.

The necessity for eliminating the barium and calcium as well as the silica, and avoiding the attack on glass vessels by sesqui-carbonate of ammonium, which introduced silicon, calcium, and sodium, led me to submit the carbonate of lithium, purified as I have just described, to the following treatment:—The salt was dissolved in sulphuric acid that had been distilled in a platinum vessel and diluted with water. The solution was evaporated to dryness in a platinum retort, and the sulphate heated to drive off the excess of sulphuric acid and render the silica insoluble. The sulphate of lithium when cold was translucent, showing white specks. When taken up by water, it made a slightly clouded solution, which was left in the platinum dish to settle. As an extra precaution, it was filtered through a double paper, which had been previously treated with dilute hydrofluoric and hydrochloric acids, then washed with pure water, and collected in a large platinum dish, where an 80 per cent solution of alcohol was added until a noticeable quantity of sulphate of lithium was precipitated, because of its slight solubility in alcohol.* The supernatant liquid was left under a bell-jar, to settle; this took a long time: then it was filtered again, and finally heated in a platinum retort to drive off the alcohol. I then precipitated the sulphate of lithium

* I ascertained these facts by dissolving 0.1 grm. of pure iron in aqua regia, and then turning the solution into almost boiling ammoniated water in a beaker. The above-mentioned ferric hydrate was collected in a filter which had been washed with a mixture of dilute hydrofluoric and hydrochloric acids, and then with water. The filter, when dried, was burnt, and the ferric oxide was put into a platinum boat contained in a carbon boat, which was brought to a dull red heat in a porcelain tube, in a slow current of hydrochloric acid gas. The volatilised ferric oxide left 0.011 grm. of perfectly white silica, containing traces of lime, but quite soluble in dilute hydrofluoric and hydrochloric acids.

* I satisfied myself that the sulphate of lithium above mentioned was mixed with a *very small* amount of barium and calcium.

in the same, platinum dish, by carbonate of ammonium prepared in another platinum dish, using for this purpose a rubber tube to introduce the ammonia and the carbonic acid gas into the water. After having heated the gelatinous precipitated carbonate of lithium for a long time, in order to make it granular (a state in which part of the decomposed sulphate re-combines, but which is necessary in order to be able to wash the precipitate), the filtrate was decanted, as much as possible was drawn off by suction, and, following the example of Berzelius, the sulphate and the sesqui-carbonate of ammonium were separated, by washing the precipitate with alcohol so diluted as not to cloud the filtrate. Berzelius recommended 99 per cent alcohol to wash a carbonate precipitated from a chloride; he had to use 60 per cent alcohol, which sensibly dissolved the carbonate, so as not to make the double sulphate of lithium and ammonium adhering to the precipitate insoluble; after washing in dilute alcohol had removed all the sesqui-carbonate of ammonium, the precipitate was poured into a funnel with a clean linen plug, connected with a filter-pump, and the washing with dilute alcohol was continued so long as the liquid clouded an acid solution of acetate of barium: this took a long time, and necessitated dissolving a noticeable amount of carbonate of lithium. When this result was reached, I put part of the precipitate into a hydrogen flame; the sodium line showed very faintly. I did not see either the red or orange lithium lines. I then heated part of the same carbonate on a platinum sheet in an oxyhydrogen blowpipe; it was completely volatilised. No trace of the calcium spectrum appeared; there was a faint suspicion of the presence of a very weak image of the barium spectrum.

The carbonate of lithium, which weighed more than 200 grms., was divided into two parts, A and B.

The part A was dissolved in dilute pure sulphuric acid; the solution was evaporated to dryness in a platinum retort, and the sulphate was melted. The salt was treated as I have described for the sulphate first made, and the resulting carbonate, after being properly washed in dilute alcohol, was entirely volatilised in an oxyhydrogen blowpipe, without which it would not have been possible to detect, by spectrum analysis, the most transient appearance of the calcium or barium spectrum. *Part of this carbonate was used to identify the luminous spectrum of oxide of lithium.*

The part B of the carbonate of lithium was heated almost to fusion in a covered platinum crucible. This salt was then suspended in water contained in a platinum retort, and subjected to a current of pure carbonic acid. When a small portion of the carbonate was dissolved, the current was stopped, and the liquid left undisturbed. After it had settled, the clear liquid was decanted, and the carbonate was submitted to a fresh wash in dilute alcohol. The washings were put back into the decanted carbonate solution, and the whole was evaporated at boiling-point in a platinum vessel down to three-quarters of its volume.

The deposited carbonate of lithium was turned out; the filtrate, when concentrated in a small platinum dish, showed a very strong sodic reaction, but showed no reaction with an acid solution of acetate of barium. A certain quantity of sulphate of sodium or lithium, capable of being removed by a barium salt, had been eliminated.

Having found these facts, part of the lithium left in the retort was dissolved. For this purpose a current of carbonic acid was passed into the water containing the salt in suspension, until it was saturated; *nine-tenths* of the carbonate in the retort was then gradually dissolved. The liquid, having become clear by standing, was boiled in a covered platinum dish, to drive off the carbonic acid and cause the deposit of the carbonate held in solution. I found thus that a litre of saturated liquid deposited from 38 to 39 grms. of carbonate of lithium. Care was taken to entirely change the filtrate, which was again saturated with lithium salts.

Having washed the deposited carbonate of lithium,

several times, with pure alcohol, it was dried and redissolved in water saturated with carbonic acid, always working with platinum dishes.

The salt which was deposited by boiling the solution, and washed again with pure alcohol, was used to check the results given by the carbonate made from sulphate, but which had not been dissolved in carbonic acid.

The results were identical as regards the lithium spectrum; the only difference noticed was that, in order to get rid of the sodium D line in the oxyhydrogen blowpipe, it was necessary to volatilise about one-half of the carbonate precipitated direct from the sulphate, whilst the same result could be obtained by volatilising one-third of that which had been treated with carbonic acid as described.

I converted part of the carbonate, which had been twice dissolved in the anhydride, into sulphate, by means of sulphuric acid distilled in a platinum vessel; *from which carbonate I had eliminated the sodium by means of an oxyhydrogen blowpipe*, changing it into an oxide. This was the sulphate I used, side by side with part of the same salt made by M. Bunsen, to study the spectrum of this salt, which was found to be identical with that of oxide of lithium.

I tried to prepare some chloride from the oxide of the same carbonate of lithium, by working with hydrochloric acid gas in platinum vessels. Although I took all the care required for eliminating sodium from oxide of lithium, the chloride made showed the sodium line *until it was entirely volatilised*, both in a Bunsen burner and in an oxyhydrogen blowpipe. I doubt whether it be possible to obtain this body, or any substance as hygroscopic as it is, so pure as not to show the sodium line on spectrum analysis. I shall support this statement by plenty of evidence, when describing the results of my researches on the compounds of calcium.

It was this impossibility of preparing a chloride of lithium which would not show the sodium line which decided me not to use this compound to compare with the spectrum of lithium.*

(To be continued.)

THE DETERMINATION OF GRAPHITE IN PIG-IRON.

By P. W. SHIMER.

THE purpose of this note is to call attention to a source of error in the determination of graphitic carbon, made by the usual method of solution in hydrochloric acid. Although the method is tedious, because of the necessary treatment of the separated carbon with caustic potash, alcohol, and ether, the text-books seem to give it preference; and it is, perhaps, used more generally than the method of solution in dilute nitric acid. Solution in hydrochloric acid usually gives higher graphitic carbon results than solution in nitric acid, and many, therefore, consider it more trustworthy, the inference being that the lower results obtained by nitric acid are due to the loss of some of the finely-divided graphite by reason of the oxidising action of the solvent. But experiments made in Dr. Drown's laboratory, about seventeen years ago, showed no appreciable oxidation of graphite in the fifteen or twenty minutes' boiling required for the solution of a sample of pig-iron.

The point I desire to bring out here is, that the high results in graphitic carbon obtained by solution in hydro-

* All the chemical researches on the carbonates, sulphates, and chlorides of lithium described above were carried on in the chemical laboratory of the "Musée de l'Industrie," at Brussels. During the removal of this laboratory to the "Palais du Midi," the collection of lithium compounds, weighing more than 2½ kilograms, was carried thither. When the laboratory of this "Palais" was burnt, the whole collection perished.

chloric acid are due to the presence in the graphitic residue of titanium carbide (see *Trans. Am. Inst. Min. Eng.*, xv., 455), and possibly of other insoluble carbides, the carbon of which is, of course, included with the graphite in the final determination. In the nitric acid method the titanium carbide is easily dissolved, and its carbon appears with the combined carbon, when the latter is determined by difference between graphitic and total carbon.

The method by solution in dilute sulphuric acid is open to the same objection as that by solution in hydrochloric acid; for titanium carbide is insoluble in sulphuric acid, and, I may add, it is also unattacked by hydrofluoric acid and by a boiling solution of caustic potash.

The following is an analysis of a pig-iron unusually high in titanium:—

	Per cent.
Silicon	3.650
Phosphorus	1.145
Sulphur	0.010
Manganese	0.226
Graphitic carbon	3.206
Combined carbon	0.128
Titanium	0.399
Iron (by difference)	91.236

100.000

The total carbon in this iron was determined by dissolving in an acidified solution of double chloride of copper and potassium, and subsequent combustion. The graphite was determined by solution in dilute nitric acid and combustion. A determination of graphite, made by solution in hydrochloric acid and combustion, gave 3.327 per cent of graphite, a result 0.121 per cent higher than that obtained by the nitric acid method. The amount of carbon combined as titanium carbide (TiC) with 0.399 per cent of titanium is 0.1 per cent, which counts as graphite in the determination by solution in hydrochloric acid. The results may be set down as follows:—

	Per cent.
Total carbon	3.334
Graphite by nitric acid solution	3.206
Graphite by hydrochloric acid solution	3.327

The error in the hydrochloric acid method falls heavily upon the resultant estimate of combined carbon, which is determined by difference, as appears below:—

	Per cent.
Combined carbon, when graphite is determined by nitric acid	0.128
Combined carbon, when graphite is determined by hydrochloric acid	0.007

An experiment was made to determine the action of boiling nitric acid (1.20 sp. gr.) on the graphite from this iron. A sample of 2 grms. was dissolved in hydrochloric acid (1.10 sp. gr.). After washing the graphitic residue with water, it was boiled gently for one hour with nitric acid (1.20 sp. gr.), with the addition of a little water from time to time, to keep up the bulk of the solution. The graphite, as thus determined, was 3.203 per cent against 3.206 per cent by direct solution in nitric acid, showing that the treatment for one hour, with boiling nitric acid, had dissolved out the titanium carbide without having attacked the graphite. The graphite in this high silicon iron, however, was coarse, and perhaps unusually resistant to the oxidising action of nitric acid. It is proposed to make similar experiments on the graphite from a variety of pig-irons.

The 0.128 per cent of combined carbon is made up as follows:—

	Per cent.
Carbon combined with 0.399 per cent titanium as TiC	0.100
Combined carbon soluble in hydrochloric acid (probably combined with iron and manganese)	0.007
Carbon possibly existing as insoluble carbide other than titanium carbide	0.021

A careful mechanical separation of a few grms. of titanium carbide was made from several pounds of this iron by use of the long, slightly inclined glass plane described in the paper before the Institute referred to above.

Besides titanium and carbon in this separation, there is some vanadium, apparently also existing as an insoluble carbide, which would account for a part of the above 0.021 per cent of combined carbon. This investigation is, however, still under way.

The writer has never encountered a pig-iron free from titanium, the amount found varying usually from 0.05 to 0.40 per cent. In irons with a coarsely crystalline fracture the cubical crystals of titanium carbide may always be found when carefully looked for. The conclusion seems to be fair that the hydrochloric acid method includes, with the graphite determined by it, the carbon existing as insoluble titanium carbide. With pig-irons containing from 0.05 to 0.40 per cent of titanium, the graphite so determined will be from 0.013 to 0.100 per cent too high, while the combined carbon will be correspondingly low.

It follows that more light would be thrown upon the condition of the carbon in pig-iron by making three determinations—viz., one of total carbon, one of the carbon insoluble in hydrochloric acid, and one of graphite by the nitric acid method. We would thus have determinations of graphitic carbon; carbon combined with iron and manganese, soluble in hydrochloric acid; and carbon combined as carbides insoluble in hydrochloric acid. In high-silicon, low-sulphur titanic irons, the insoluble form of combined carbon exceeds the carbon existing as soluble carbides of iron and manganese. It is important to know how the carbon is combined. One-tenth per cent of carbon combined with titanium in the condition of disseminated microscopic crystals, probably has no effect on the hardness of pig-iron; while the same amount of carbon, combined with iron and manganese, would have an appreciable hardening effect. Practically, therefore, it may be desirable to have the carbon existing as carbides insoluble in hydrochloric acid appear with the graphite as determined by the hydrochloric acid method, although the actual graphite can be determined only by solution in nitric acid. At all events it is essential to know by what method graphite has been determined, in order to draw conclusions from determinations of graphitic and combined carbon in pig-iron.—*Journ. Amer. Chem. Soc.*, vol. xvii., p. 873.

ON THE OXIDATION OF SOME GASES WITH PALLADINISED COPPER OXIDE.*

By E. D. CAMPBELL.

In the work heretofore done on the combustion of gases where the well-known influence of finely divided palladium upon the ignition of gases has been taken advantage of, the oxygen for the combustion of the gas under examination has been introduced either as pure oxygen or diluted with nitrogen in the form of air. It was thought not impossible if palladium in sufficiently fine form and evenly distributed could be introduced into a solid reagent capable of giving up oxygen to combustible gases, that the temperature at which gases containing hydrogen would burn, might be lowered below the combustion-point in the absence of palladium, and that the differences in the temperatures of combustion of various gases might lead to a system of fractional combustion.

Copper oxide, being one of the most common reagents for combustion, and having the great advantage over most others of being easily re-oxidised after reduction, was thought to be the most desirable substance to work upon.

* Contributions from the Laboratory of Analytical Chemistry of the University of Michigan. From the *American Chemical Journal*, vol. xvii., No. 9, November, 1895.

Copper oxide, containing palladium very finely divided and evenly distributed throughout, was prepared in three ways; of these the first by which the oxide used in the combustion shown in the table was made, was as follows:—

An alloy was prepared by melting 600 grms. of fine copper and then adding 6 grms. of palladium. After melting this alloy was cast into a cold iron mould, then broken up and re-melted at a temperature nearly approaching the melting-point of palladium (considerably above that of copper), then quickly re-cast into cold iron moulds, the strips so cast being about 12 m.m. wide and 5 m.m. thick. Palladium did not seem to alloy very readily with copper, so that it was necessary to re-melt at a high heat and cool quickly to prevent the palladium from distributing itself in the form of a fine network, which rendered the alloy brittle when attempts were made to roll it. By re-melting at a high heat and quickly cooling an alloy was produced in which the palladium was evenly distributed, and which rolled as easily as pure copper. The strips of alloy thus produced were annealed like pure copper, then rolled until the thickness was reduced to 0.3 m.m., the width remaining about the same. These strips were then cut transversely into pieces 1.5 m.m. wide, thus giving small pieces 12 m.m. long, 1.5 m.m. wide, and 0.3 m.m. thick. About 160 grms. of this alloy was introduced into a combustion-tube of 16 m.m. internal diameter, the alloy being retained in position at both ends by plugs of copper gauze. The column of alloy was 34 c.m. long. The combustion-tube so prepared was placed in an ordinary Bunsen combustion-furnace, brought to a moderate red heat, and purified oxygen passed through as long as it was taken up.

Second Method.—In the course of the work, owing to frequent reduction and re-oxidation of the copper, and to handling of the oxide in filling or emptying tubes, a considerable amount of fine oxide accumulated which could not be used as it was without choking the tube. This fine oxide was ground until it would pass through a 100-mesh sieve, mixed with thick mucilage to a rather stiff paste, and pressed by means of a sodium press into wire a little less than 2 m.m. in diameter. This wire, after it had become dry, was broken into pieces about 10–12 m.m. long, introduced into a platinum crucible, and heated to a moderate red heat until all volatile matter ceased coming off. The wire so produced was strong enough to retain its form perfectly while introducing it into a combustion-tube in which it could be completely oxidised by means of oxygen at a red heat.

Third Method.—This method was not worked out until the combustions shown in the table were completed, but it is recommended as the best method for the purpose of preparing the oxide, as it is much simpler than either of the previous methods, and the oxide prepared by it we have shown by quantitative combustion of hydrogen is fully as efficient as that produced by the first or second method. The method is as follows:—3 grms. of palladium wire was dissolved in a moderately-sized casserole by means of 40 c.c. of nitric acid (sp. gr. 1.42), to which was added 10 c.c. of hydrochloric acid (sp. gr. 1.20). After evaporating to dryness on the water bath the palladium was brought into solution with 10 c.c. of nitric acid, 3 c.c. of hydrochloric acid, and sufficient water to bring the volume to 60 c.c. Into this solution was introduced 300 grms. of pure copper oxide, previously ground to pass through a 100-mesh sieve. This produced a very stiff paste, which after thorough mixing was dried at 120° and again ground to pass through a 100-mesh sieve. The fine ground oxide so produced was then mixed with mucilage, pressed into wire, dried and ignited like that in the second method of preparation.

In order to control the temperature of the tube at any time a special form of air jacket was made, in two halves, so that it could be put on when the combustion-tube was used for combustion, or removed when it was desired to re-oxidise the copper without disturbing the position of

the tube. The jacket consisted of two halves of a heavy brass tube 3 m.m. thick, 52 m.m. internal diameter, and 48 c.m. long; this internal diameter allowed the jacket to surround the combustion-tube and its gutter and still leave a clear space of 5 to 7 m.m., thus heating the tube entirely by radiation. The thickness of the inner brass tube also tended to equalise the temperature and to prevent sudden variations. The two halves of this inner brass tube were joined at both ends to an outer heavy sheet-iron tube, leaving between the tubes an annular space of 7 m.m. The two halves of outer sheet-iron tube came together on the under side in the form of a lap joint, and were prolonged on the upper side so as to be supported by means of metal pins on both sides of the double horizontal bar at the top of the furnace usually used to keep the tiles apart. Through the double bar at the top of the furnace, and through three holes in the inner brass tube, were introduced three nitrogen-filled thermometers capable of registering 460°. These thermometers reached to and rested on the inner combustion-tube. In addition to this jacket on each side of the furnace were provided two sheet-iron guards to prevent currents of air and to maintain a steadier heat. In addition to these a heavy sheet-iron gutter, 54 m.m. wide and 48 c.m. long, was curved to fit the under side of the outer jacket, and when wired to it could take the direct heat of the flame and prevent the burning out of the outer jacket. This gutter was found necessary when working at the higher heats. Thus provided, the inner combustion tube was so placed that it was heated by radiation from the heavy inner brass tube, which was in turn heated by radiation from the outer sheet-iron jacket. In this way a steady even temperature of the combustion-tube could be maintained at any temperature up to 450°, and the entire jacket could be easily removed, the tiles put back in their usual place, and the copper re-oxidised without disturbing the combustion-tube.

In determining the initial combustion-point of any gas, a moderate flow of the pure gas was kept passing through the combustion tube, to the farther end of which was attached a small tube containing glass-wool sprinkled with anhydrous cupric sulphate, for the detection of moisture, followed by a U tube containing a clear solution of calcium hydrate for the detection of carbon dioxide. The temperature of the tube was gradually raised, the three thermometers being kept within a range of 5° until a test for moisture and carbon dioxide was obtained. As soon as this was done in any case the supply of gas was shut off and pure dry air drawn through the tube, the temperature allowed to fall below the ignition-point, the gas turned on again, and the temperature again carefully brought up until a second test was obtained. In gases containing both carbon and hydrogen, a test for carbon dioxide was obtained always a little in advance of that for moisture. This difference is probably accounted for by the greater sensitiveness of calcium hydrate for carbon dioxide than that of hydrous cupric sulphate for moisture. In the table of results the limits of temperature given include those at which distinct test for both moisture and carbon dioxide were obtained. In determining the ignition-point of a gas it was also found necessary to use the combustion-tube after it had been used for a quantitative combustion, since a freshly re-oxidised tube was found to contain small amounts of palladious oxide, which gives up its oxygen very much more readily than the copper oxide, and which would consequently make the ignition-point apparently much lower than its true value.

For the quantitative combustion of gases, the inlet end of the combustion-tube was connected to a T tube provided with a three-way stop-cock, by means of which either the pure dry gas under examination could be introduced into the tube, or by reversing the cock pure dry air or oxygen could be drawn or forced through the tube for the purpose of sweeping forward the products of combustion or for re-oxidising the copper when desired.

(To be continued).

NOTICES OF BOOKS.

The Factory Acts. By the late ALEXANDER REDGRAVE, C.B., Her Majesty's Chief Inspector of Factories, &c. Sixth Edition. Including the Act of 1895. By JESSE A. REDGRAVE, One of Her Majesty's Inspectors of Factories; and H. S. SCRIVENER, M.A. Oxon, of the Middle Temple, Barrister-at-Law. London: Shaw and Sons, and Butterworth and Co. 1895. Pp. 356.

THE legislation concerning factories and workshops is not only voluminous in itself, but has been complicated by the partial repeal of certain Acts. Hence the work before us is useful not merely to manufacturers who wish to know when they are obeying the law, but also to solicitors and to the inspectors themselves. No fewer than nine Acts of Parliament are here quoted in full; nine others are given in part.

It is satisfactory to find that the expressions "factory" and "workshop" are now officially defined. It is also satisfactory that certain judicial decisions are given touching questions which might furnish scope for quibbling. The phrase "a Secretary of State," or, at greater length, "one of Her Majesty's principal Secretaries of State," might be judiciously altered. The "Home Secretary" would in every case be a happier expression, except where the manufacture of explosives, &c., for the War Department is concerned. We notice that print-works, bleach- and dye-works, chemical- and colour-works are admitted to be non-textile factories, and are consequently exempted from certain regulations which would then be useless and annoying.

It appears that a special notice of any case of lead-, phosphorus- or arsenic-poisoning, or anthrax, is a new and justifiable provision. But we are informed, in a note, that the Secretary of State may apply it by order to any disease occurring in a factory or workshop. Now, it would not be difficult to name diseases the occurrence of which has no connection with the sanitary conditions of a factory or with the processes there carried on.

A provision given on p. 236 will, we may hope, touch manufacturers of clothing who give out materials to be made up in unsanitary localities.

In fine, the Acts and provisions here quoted or abstracted seem to be just and needful, and the work before us may hence be regarded as valuable and deserving recommendation.

Practical Inorganic Chemistry. By G. S. TURPIN, M.A., D.Sc., Head Master of the Intermediate and Technical School, Swansea. London and New York: Macmillan and Co. 1895. Pp. 158.

IT is to be hoped that some time the abundant treatises on the various sciences, and especially on chemistry, will begin to germinate and yield a harvest. As a rule, like the little volume before us, they contain nothing erroneous in fact or mistaken in generalisation. But for all this we are left in painful doubt as to their *raison d'être*, and we are driven to hope that the issue of elementary treatises might be suspended pending the avatar of some capital discovery, such, *e.g.*, as the decomposition or the synthesis of some one of the elements.

Helps to Health and Beauty. Two Hundred Practical Prescriptions. By A PHARMACEUTICAL CHEMIST. London: James Clarke and Co. (Fleet Street). 1895. Pp. 117.

THIS little work is of a character rarely noticed in our pages. The substances here mentioned, whether medicines or cosmetics, are, with rare exceptions, not combinations, but mixtures. The author, however, is decidedly master of his subject. We must note, as an instance in proof, that he insists on the superiority of English oil of

lavender—the growth of Mitcham or Sandy—to that of foreign growth for the manufacture of perfumes. The recommendation of the florets of *Pyrethrum roseum* as an insecticide is strongly to be approved of. It is strange that, whilst in the colonies of Australia and South Africa country fit for the cultivation of the plant exists in square miles, the inhabitants still submit to be bitten, stung, and buzzed about by noxious insects.

It might have not been amiss if the author had called attention to the value of marsh rosemary (*Sedum palustre*) as a preservative against mosquitoes and sand-flies.

The Physiology of the Carbohydrates: an Epi-criticism. By F. W. PAVY, M.D., LL.D., F.R.S., Fellow of the Royal College of Physicians, &c. London: J. and A. Churchill. 1895. Pp. 141.

THIS book is concerned with a controversy concerning the "glycogenic theory." Does the liver, as Dr. Noel Paton contends, generate sugar? or is this viscus, as Dr. Pavy shows, a sugar destroyer? The question is complicated by the fact that Dr. Paton's support of the glycogenic theory has found its way into the *Philosophical Transactions of the Royal Society*, in a memoir not quite free from personalities. The President and Council have certainly, in a private letter to Dr. Pavy, expressed their regret that this paper should ever have been suffered to appear; but this does not undo the fact and the effects of its publication. Dr. Pavy, as regards the "glycogenic theory," appears to be in the right.

Molecules and the Molecular Theory of Matter. By A. D. RESTEEN, S.B. Boston (U.S.A.) and London: Ginn and Co. 1895. 8vo., pp. 223.

THE author of this ably-written work opens his Preface with the remark that "In the multiplication of popular books on scientific subjects the molecular theory of matter seems to have been strangely neglected." Hence we may fairly infer that Mr. Resteen intended to produce a treatise which should be intelligible to the cultivated public, and at least to men of Science whose speciality is not mathematical. How such works might be written on physical subjects it may be seen from the examples set by Tyndall. Our author, however, if such was his intention, has failed in its execution. His work, however valuable, will not be as a whole available to any one who has not a full command of the resources of the higher mathematics. It must further be kept in mind that he treats of molecules in their physical aspect, referring the reader for the chemical phase of the subject to the writings of Meyer, Remsen, Ostwald, and Mendeleeff.

After a section on general considerations, in which a distinction is drawn between molecules and atoms, we proceed to the kinetic theory of gases. Here we have an exposition of the law of Avogadro and Boyle, and a survey of the phenomena of high vacua, with an appreciative notice of the researches of Mr. Crookes, F.R.S., in this direction.

The molecular theories of liquids and solids form the subject of two succeeding sections. In the remaining sections we have a discussion of molecular magnitudes and of the constitution of molecules. The conclusion reached is, that "something is known of the constitution of gases, a little of the constitution of liquids, and almost nothing, for certain, of solids." About the constitution of molecules, and the mechanical nature of intermolecular forces, nothing whatever is yet known.

The hypothesis of Prout is, as we need scarcely say, rejected. On the ultimate unity of matter Mr. Resteen does not pronounce decidedly; nor does he speculate on the possible origin of the elements. Yet that he is not devoid of the scientific imagination we may gather from his speculations on the conservation of weight. He does not see any warrant for the ordinary assumption "that when an atom whose weight is A combines with another

atom whose weight is B the weight of the resulting molecule is universally and necessarily $A+B$." He does not ignore the consequences which must follow from his suggestion, if it should ever be verified; nor does he adduce any phenomena in its support. He thinks that his hypothesis explains both the existence of elements and the slight deviation from integral values which we find in their atomic weights. Mr. Resteen ascribes the entire merit of the discovery of the "Periodic Law" to Meyer and Mendeleeff, and rejects the analogy suggested between the periodic law of the elements and the astronomical law of Bode.

Could the work before us be divested of its mathematical scaffolding it would merit, and doubtless receive, a very general appreciation.

CORRESPONDENCE.

ON THE PLACE OF HELIUM IN THE CLASSIFICATION OF ELEMENTARY SUBSTANCES.

To the Editor of the Chemical News.

SIR,—Mr. Gladstone complains of the tone of my criticism which has been adopted to meet his peculiar controversial methods in dealing with questions of vital importance to the future progress of chemical science. As he appeals to chemists who are interested in the questions of priority, raised incidentally in this discussion, to judge for themselves, it will facilitate the enquiry if I point out that Dr. Gladstone, in the reference to his paper in the *Philosophical Magazine*, May, 1853, has put forward the old atomic weights, 16 and 24, as anticipating the same numbers in my table, which, as every chemist knows, are double the old atomic values.

The vertical series of constant differences, 16, 16, 24, 24, 24, advanced by Dr. Gladstone as new in the year 1883, are the same as those in the series H_{2n} of my table of 1878, as shown in my letter to the *CHEMICAL NEWS* of December 13th last. As there is an absolute parallelism between the constant differences of the atomic weights of the first and second series, H_n , H_{2n} , Dr. Gladstone has himself furnished full proof that the differences of the atomic weights of the first group or series in Mendeleeff's table and in my own do not increase as we go downwards as he alleged.

Now that the question of the place of helium in the classification of the elements is definitely raised in the *CHEMICAL NEWS*, I will, with your permission, make a few remarks on the periodicity of chemical properties which is supposed to exist when the elements are arranged in seriatim order of their atomic weights. In a paper which I read before the Manchester Literary and Philosophical Society on December 11th, 1894, it was proved that, when such an arrangement of the atomic weights was rightly adhered to, the idea of recurring properties or periodic functions has no real foundation in nature. It was also demonstrated by means of two tables, A and B, that, when a new element x was brought into the series, the order of the whole system vanished, and that the predictions of the properties of unknown elements, so far from being the result of the so-called periodic law, were made in spite of it.

In the *CHEMICAL NEWS* of December 20th last another attempt is made, by Mr. R. M. Deeley, to bring helium into a periodic system. Tables I. and II. in his communication demonstrated the fallacies involved in the periodic system so much more forcibly than the demonstration given in my paper, that a first examination of these tables left the impression that Mr. Deeley was a humorist adopting an ironical method of bringing the periodic system into ridicule. His papers in the *Trans-*

actions of the Chemical Society, to which he refers, and his last communication to the *CHEMICAL NEWS* show, however, that Mr. Deeley is an earnest student, endeavouring to reconcile the facts of his science with the impossibilities involved in a classification based on an imaginary periodicity of chemical properties when the elements are arranged in the proper order of their atomic weights. Mr. Deeley's papers and tables deserve the serious attention of all who are interested in the progress of chemical philosophy.—I am, &c.,

HENRY WILDE.

January 14th, 1896.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 25, December 16, 1895.

Composition of the Flours furnished by Grinding Soft Wheats and Hard Wheats in Cylinders.—Aimé Girard.—From the analytical and practical study of the produce of three grindings executed under the superintendence of the Commission, it appears distinctly that the limit of the yield in flour fit for the manufacture of white bread, porous, well-risen, and easily digestible, as modern consumption requires, lies between 60 and 65 per cent of the weight of the wheat. Beyond this point, we find about 5 per cent of mealy product, decidedly acid, and calculated to yield only compact loaves, flat, with a greasy crumb, dark coloured, loaded with water, and difficult of digestion.

Direct Combination of Atmospheric Nitrogen with the Metals in the form of Magnesium, Aluminium, Iron, Copper, &c., Nitrides.—A. Rossel.—The author, in conjunction with Léon Frank, has established that it is not the same if we heat pulverised calcium carbide with magnesium in powder to dull redness either in a porcelain crucible or in a tube in which the atmospheric air circulates freely. The reaction takes place in a regular manner—layers of pulverised calcium carbide and of magnesium in fine powder. The product, freed mechanically from the lime, leads on analysis to the formula Mg_3N_2 . The residue in the crucible contains as much as 23.8 per cent of nitrogen, obtained from the atmospheric air. Aluminium, zinc, iron, and even copper, if treated in the same manner, give similar reactions, forming products decomposable by water, and more readily by dilute potassa lye. These reactions are an additional proof, as Moissan has pointed out, that at the epoch of the formation of the earliest geological strata nitrogen did not exist in the free state, but in combination with metals.

Preparation and the Properties of Crystalline Chromium Sulphide.—A. Mourlot.—The author shows that the sulphide formed by the action of hydrogen sulphide upon metallic chromium is a protosulphide. By an increase of temperature, he has effected the crystallisation of this substance. The sulphide has a great stability.

Lithium Subchloride.—M. Guntz.—On heating in a nickel crucible, and in a current of hydrogen, 27.4 grms. $LiCl$ and 4.7 grms. metallic lithium to dull redness, we obtain a melted product, slightly greyish, very hard, and homogeneous. It has the composition Li_2Cl , and decomposes water as readily as does lithium itself. The metal absorbs nitrogen very readily.

Certain Novel Safranines.—G. F. Jaubert.—The author has undertaken to produce the simplest possible safranines containing an alcoholic radicle linked to azinic nitrogen.

He has formed a methylic derivative, metho-safranin; an ethylic compound; etho-safranin, and two naphthyl derivatives, α and β naphtho-safranines.

Study of *Aspergillus Orizæ*.—E. Sorel.—The author has verified the accuracy of the observation of Jubler and Joergenson that *Aspergillus orizæ* is transformed into a *saccharomyces*.

Researches on the Influence of Electricity on the Development of the Embryo of the Fowl.—Camille Dareste.—The germ is not affected in its material constitution by electric influences which destroy adult animals of a certain bulk (?) But the germ is nevertheless modified, in a majority of cases presenting teratological phenomena.

Study of the Action of various Radiations of the Solar Spectrum upon Plants.—C. Flammarion.—The observations were made upon sensitive plants growing respectively in houses of red, green, and blue glass; a house of ordinary white glass serving as a check. The growth in height followed the order—red, green, white, blue. In vigour and activity of vegetation, the order was—red, white, green, blue. Under blue glass the vegetation was very feeble. The action of red light is compared to that of a chemical manure.

No. 26, December 23, 1895.

This issue gives the account of the usual Public Session of the Academy, with obituary notices of deceased Members and Associates. Pasteur received the well-merited eulogium, and there was also honourable mention of Verneuil, of Larrey, of Cayley, Dana, Vogt, Lovén, Hellriegel, and Huxley. The last-mentioned *savant* was especially characterised as a reformer of higher education, as one who had reproached the ancient universities of Oxford and Cambridge for having forsaken their true task, and from being nurseries of study and research, they have sunk down to be boarding-schools for wealthy youths. The speaker further denounced the small share of attention granted to Natural Science. The Grand Prize for the Physical Sciences has been awarded to Charles Brongniart for his paleontological researches on the coal-beds of Commeny. The Biennial Prize has been allotted to M. Raoult for researches on molecular precipitations, and their application to the sanitation of unwholesome industries. The Leconte Prize has been awarded to Lord Rayleigh and Professor Ramsay for their well-known researches on the constitution of atmospheric air. The prize offered by Alberto Levi for a remedy for diphtheria has been granted to Dr. Behring.

MEETINGS FOR THE WEEK.

MONDAY, 20th.—Society of Arts, 8. (Cantor Lectures). "Alternate Current Transformers," by Dr. J. A. Fleming, F.R.S.

TUESDAY, 21st.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.

— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Photographic, 8.

WEDNESDAY, 22nd.—Society of Arts, 8. "Supply of Sea-Water to London," by Frank W. Grierson.

— Geological, 8.
THURSDAY, 23rd.—Royal, 4.30.
— Chemical, 8. Helmholtz Memorial Lecture, by Prof. G. F. Fitzgerald, F.R.S.

— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Dante," by Philip H. Wicksteed, M.A.

FRIDAY, 24th.—Royal Institution, 9. "Ludwig and Vitalism," by Prof. Burdon Sanderson, M.D., F.R.S.

— Physical, 5. Exhibition of some Geometrical Instruments, by E. Scott and Signor Monticelo. "On Resultant Tones," by J. D. Everett. Experiments with Incandescent Lamps, by Sir David Salomons.

SATURDAY, 25th.—Royal Institution, 3. "The Valley of Kashmir," by Walter R. Lawrence, I.C.S.

KING'S COLLEGE; LONDON.

Laboratory Attendant required in the State Medicine Laboratory.—Apply to WALTER SMITH, Esq., Secretary, King's College, Strand, W.C.

Chemist and Assayer Wanted; well up in methods for estimation of Copper, Antimony, Lead, Gold, and Silver.—State age, qualifications, experience, references, and salary required, to A. B., The Sheffield Smelting Co., Lim., Sheffield.

Wanted, a trained Chemist for the Dye-work of a firm dyeing first-class fancy cotton goods; must be capable of superintending dyeing operations and undertaking Analytical Work: a Fellow of the Institute preferred.—Apply, stating age, qualifications, references, and salary, to D. W., CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

Wanted, competent Man, with practical experience in Metallurgy of Silver, Lead, and Copper, dry and wet methods; to superintend Works operations and act as Assayer and Chemist.—Full particulars to "Provincial," CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

Wanted, a Manager for Acid Industries in South Africa. Competent Man required for Administration. Thorough knowledge of Sulphuric Acid manufactory and branch industries indispensable. Experience in treatment of Gold Ore by chlorination preferred. Only first-class men need apply. Testimonials and references required. State salary.—Letters, G. S., care of A. Siegle, 30, Lime Street, London, E.C.

NOTICE TO ANALYSTS AND LABORATORY DIRECTORS.

Best METHYLATED SPIRIT, manufactured by A. & J. WARREN, Wholesale Druggists, Dealers in Chemicals for Analytical Work, and Methylated Spirit Makers, 23 and 24, Redcliffe Street, Bristol. For Four-pence a Pamphlet on Methylated Spirit, written by Algernon Warren, is obtainable from the Publisher J. W. ARROWSMITH, Quay Street, Bristol; and SIMPKIN, MARSHALL, HAMILTON, KENT, and Co., Ltd., London.

NOTICE.

JOHN CLIFF & SONS, EXCHANGE CHAMBERS, LEEDS, wish to SELL (preferred) or LET their Chemical Stoneware and Pipe Pottery, at Runcorn, upon Manchester Ship Canal (and scheduled for purchase), with view of OPENING AT LEEDS, near their headquarters.

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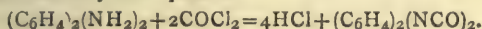
VOL. LXXIII., No. 1887.

ACTION OF DIPHENYLENE DI-ISOCYANATE UPON AMIDO-COMPOUNDS.

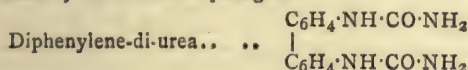
By H. LLOYD SNAPE, D.Sc., Ph.D.

THE preparation of diphenylene cyanate I described some years ago (*Journ. Chem. Soc.*, xlix., 253); and I then showed that, like phenyl iso-cyanate, it readily entered into combination with alcohol and phenol respectively, forming the corresponding carbamates. It seemed probable that the similarity would extend to the behaviour of the new cyanate towards ammonia and aniline; and this I have found to be the case.

The method by which I obtained the dicyanate consisted in heating the benzidine hydrochloride (the salt being preferable to the base, because it is more stable) successively in benzoic acid and diphenylamine vapours, in a current of phosgene gas, the ultimate reaction being represented by the equation—



In repeating this, to prepare a fresh quantity of the cyanate for my present experiments, I found that it was unnecessary to regulate so rigidly the temperature, and that even a better yield could be obtained on heating the benzidine salt in a rapid current of phosgene (generated by very gently heating its solution in toluene) by a smoky gas flame, allowing the temperature to gradually rise until the deposition of solid cyanate in the neck of the tubulated retort employed, ceased. The yield still leaves much to be desired, owing apparently to the intermediate formation of diphenylene urea, which is only partially attacked by the excess of phosgene.

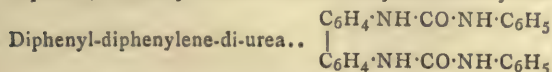


Ammonia gas was conducted into an ethereal solution of the diphenylene dicyanate, when a white crystalline compound at once separated. This was purified by solution in concentrated sulphuric acid and precipitation by water, and was submitted to analysis.

0.076 grm. yielded 13.6 c.c. N at 15° and 761 m.m.

	Per cent N.
Found	20.98
Required for $C_{14}H_{14}N_4O_2$	20.74

The substance possessed all the characteristics named by H. Schiff (*Berichte d. D. Chem. Gesell.*, xi., 833) of that obtained by him by heating benzidine with urea. He does not give the structural formula of the compound nor his analytical data, but merely states that the composition may be thus described, $C_{12}H_8(NH_2)_2 + 2CO(NH_2)_2 = 2NH_3$. This, however, is not discordant with the formula given above; and the substance prepared by him is, as I had expected, evidently identical with that synthesised by me.



Dilute ethereal solutions of diphenylene dicyanate and aniline were mixed together, and after an interval of one or two minutes, a white precipitate suddenly separated. This was soluble in hot aniline and, even at ordinary temperatures, in sulphuric acid. From the former solution it separated on cooling in small crystals, but from the latter solution it was precipitated, on the addition of

water, in amorphous gelatinous form. The compound proved to be, as I had anticipated, identical with that obtained by B. Kühn (*Berichte d. D. Chem. Gesell.*, xviii., 1478) from benzidine and phenyl isocyanate. Analysis gave the following result:—

0.106 grm. yielded 12.3 c.c. N at 15° and 754 m.m.

	Per cent N.
Found	13.48
Calculated for $C_{26}H_{22}N_4O_2$	13.27

Hence diphenylene dicyanate behaves like other isocyanates towards amido-compounds.

University College of Wales, Aberystwyth.

ELECTRO-DISSOLUTION AND ITS USES.

By H. N. WARREN, Research Analyst.

ON the same principle that electro-dissolution is used for the estimation of combined carbon in steel, &c., I have lately varied the experiment by introducing—instead of steel—iron containing a certain percentage of boron, and, having connected the respective boride with the positive pole of a powerful battery, and to the negative a plate of platinum, using as a solvent dilute sulphuric acid, I observed, after the lapse of about twelve hours, that the iron had entirely passed into solution, and a considerable amount of brownish precipitate had collected at the bottom of the vessel, intercepted by flakes of graphite and carbon. The precipitate, having been collected on a filter-paper, washed, and dried, proved on examination to be amorphous boron, containing graphite and other impurities, which had become chemically introduced during the preparation of the boron compound. The boron was next introduced into a small clay crucible, and intensely heated in a current of hydrogen gas, for the purpose of rendering it more dense and destroying its pyrophoric properties; and was, lastly, introduced into a combustion-tube and heated to redness in an atmosphere of carbonic anhydride, in order to separate the carbon; pure boron was finally obtained.

In like manner silicon-eisen, containing 9 per cent of silicon, was treated, but the result was not so satisfactory; only a small quantity of silicon separates in the uncombined form, the greater quantity separating in the form of silica, SiO_2 , the amorphous silicon being apparently more prone to oxidation than the boron so obtained.

Ferrous sulphide was next similarly treated, and gave, after the lapse of a few hours, a copious blackish precipitation of sulphur, and possessing properties similar to the sulphur obtained by dissolving sulphides, such as cupric sulphide in dilute nitric acid,—in all other respects resembling common sulphur. Phosphides of iron, zinc, &c., were next introduced, and gave, besides carbon and other impurities, a residue containing a large percentage of phosphorus, which differed from ordinary phosphorus with respect to its insolubility in carbon disulphide, and resembled the reaction afforded in the case of silicon-eisen, rather than that of the boron compound, inasmuch that a large quantity of phosphorus had passed into solution. A rod of impure copper—containing arsenic, iron, zinc, and other impurities—was next substituted, using hydrochloric acid as a solvent in place of sulphuric acid. In the course of a day the copper had entirely dissolved and precipitated itself in the negative electrode, the impurities remaining in solution.

The copper, after having been washed, dried, and weighed, gave identical results with regard to percentage with a careful gravimetric estimation.

I have lately used this method, and obtained excellent results with respect to the analysis of commercial copper, especially in the estimation of small quantities of arsenic, thus enabling the experimenter to form his investigation

on a much larger quantity than when precipitation is resorted to, at the same time avoiding the precipitated copper carrying down with it the arsenic. I have, in this manner, detected arsenic in commercial copper when all other methods have totally failed. Electro-dissolution may also be employed in the preparation of unstable compounds, such as stannic nitrate, potassic ferrate, ferric acetate, which are decomposed on the application of heat, and in some instances have succeeded by the means which follow of crystallising the resulting compound.

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CONTRIBUTIONS TO THE SEPARATION OF MERCURY FROM THE METALS OF THE ARSENIC AND COPPER GROUP.*

By CARL VON USLAR.

(Concluded from p. 29).

Separation of Mercury from Bismuth.

THE bismuth was always weighed as oxide. Before weighing it was again ignited and allowed to cool in the exsiccator. The separations, as in the case of the other metals, were effected both in a nitric and a hydrochloric solution. It was found, however, that a separation in a nitric solution gave values too low by from 1 to 2 per cent.

In order to prevent as far as possible a separation of basic bismuth chloride, a rather larger quantity of hydrochloric acid was employed, ranging from 20 to 30 c.c. The bismuth oxide, like the mercuric chloride, was first dissolved in the corresponding quantity of hydrochloric acid, then carefully diluted with hot water to 150 c.c.; the phosphorous acid was added to the cold liquid, and the whole digested in the manner already indicated.

The precipitate formed was filtered, washed with hot water containing hydrochloric acid (30 c.c. hydrochloric acid to 250 c.c. water) until no reaction of bismuth can be detected, and the liquid is once more mixed with phosphorous acid and digested. After prolonged standing there appeared a slight second precipitate.

The two precipitates were united, oxidised, and further treated as already described. On treatment with potassium-sulphide-potassium-hydroxide, there remained undissolved a slight brownish black precipitate of bismuth sulphide. It was afterwards united with the main quantity of the bismuth sulphide.

The filtrate containing the bismuth was first precipitated with hydrogen sulphide, and the precipitate of bismuth sulphide was tested for the presence of mercury sulphide by digestion with the mixture of potassium sulphide-potassium-hydroxide. Mercury was not detected in any of the precipitates.

The precipitates of bismuth sulphide were placed in a beaker and treated with hot concentrated nitric acid until the residues of the filters appeared of a pure white. The mixture was then diluted with hot water filtered off from the remnants of the filters, washed with hot dilute nitric acid until no blackening was produced on treatment with sulphuretted hydrogen water.

The filtrate was then evaporated down to a very small volume, slightly diluted with hot water after the expulsion of the nitric acid, neutralised with ammonia, and the bismuth was entirely precipitated at a boiling heat with a mixture of ammonium hydroxide and ammonium carbonate (in equal parts) avoiding excess, which has a solvent action upon bismuth carbonate. The precipitate, when well washed and dried, is placed upon glazed paper, the remnants of bismuth carbonate adhering to the filter are dissolved in concentrated nitric acid, the solution is evaporated in a weighed porcelain crucible to dryness and

gently ignited. It is then allowed to dry, the bulk of the precipitate is added and ignited until the weight remains constant.

Where the quantities of hydrochloric acid were small (20 or 25 c.c.), the mercurous chloride had no grey colour, but with 30 c.c. there was a considerable reduction to metal.

In presence of bismuth mercuric chloride is not completely precipitated by phosphorous acid in a nitric solution. If we use a hydrochloric solution the precipitation is perfect, but small quantities of bismuth compounds are also thrown down.

Separation of Mercury from Lead.

In case of lead the separation in a nitric solution is preferable. In a hydrochloric solution the precipitation of mercurous chloride was complete, but it was accompanied by small quantities of lead chloride.

Separation of Mercury from Arsenic.

In all experiments the arsenic was weighed out as teroxide. Two experiments were undertaken, respectively in hydrochloric and in nitric solution. The arsenic teroxide was oxidised by means of nitric acid, the solution evaporated on the water-bath nearly to dryness, and thus all the nitric acid was expelled. The mercuric chloride and the requisite quantity of acid were then added, and the operation was conducted exactly as with metals of the copper group. When hydrochloric acid was used the deposit of mercurous chloride indicated a partial reduction to the state of metal. The precipitate was found to be free from arsenical compounds.

The arsenic present in the filtrate was precipitated with hydrogen sulphide. After complete saturation the liquid was allowed to stand for 24 hours in a warm place, the precipitate was collected, sulphuretted hydrogen was again passed into the filtrate, and after prolonged standing the second deposit of arsenic sulphide was united with the main precipitate. After perforating the filter the precipitate is washed into a beaker with boiling water, to which a few c.c. of potassium sulphide and potassium hydroxide have been added, and further digested with about 20 c.c. of the above mixture until the whole is dissolved. The liquid is then diluted with water, boiled up and mixed with ammonium chloride. As there ensued no separation of mercury sulphide the arsenic was precipitated from the clear liquid as arsenic pentasulphide by acidification with hydrochloric acid. The precipitate was then collected on a filter, dissolved in hot ammonium sulphide, the solution heated in a porcelain capsule on the water-bath until the ammonium sulphide is decomposed, and the arsenic sulphide which separates out in crusts is oxidised with potassium chlorate and hydrochloric acid.

The sulphur separated out is removed by filtration, the filtrate supersaturated with ammonia, and the arsenic is precipitated as magnesium-ammonium arseniate by means of an ammoniacal solution of magnesium chloride. After standing for 24 hours the precipitate thus obtained is re-dissolved in hydrochloric acid and again precipitated with concentrated ammonia.

Separation of Mercury from Antimony.

Three experiments were made, two in a hydrochloric, and a third in a nitric solution. The antimony was weighed as teroxide after it had been slightly heated in a current of carbon dioxide and allowed to cool. The oxidation of the antimony oxide was effected by means of nitric and hydrochloric acid. The teroxide was dissolved in concentrated hydrochloric acid, and concentrated nitric acid was then gradually added until all the antimony teroxide is oxidised. The excess of nitric acid is expelled, and the liquid is evaporated almost to dryness. A little tartaric acid (1.5 grms.) is then added in order to retain the antimonious acid in solution when diluted with water. The mercuric chloride was then dissolved in water with the addition of the requisite quantity of acid. In the nitric experiment it was found necessary first to dissolve

* *Zeitschrift für Analytische Chemie*, vol. xxxiv., p. 391.

the antimonie acid in a little hydrochloric acid before adding the nitric acid. The entire liquid was then made up to 150 c.c., the phosphorous acid was added, and the operation concluded as already indicated. The results show that the separation of mercury from antimony gives good results either in a hydrochloric or in a nitric solution.

Separation of Mercury from Tin.

The experiments showed that a perfect separation of mercury from tin cannot be effected by the method in question.

Separation of Mercury from Cadmium, Bismuth, Copper, Lead, Arsenic, and Antimony.

Two analyses were effected in which only the mercury was determined; 0.2 grm. of each metal was weighed out.

Arsenic and antimony teroxides were first oxidised by means of hydrochloric and nitric acids, and there was added a solution of cadmium oxide, copper oxide, and bismuth oxide in 20 c.c. hydrochloric acid, and the mercuric chloride. The liquid was diluted to about 130 c.c., and lastly an aqueous solution of the lead nitrate was added.

After small quantities of lead chloride deposited had been re-dissolved by a gentle heat, 10 c.c. of the solution of phosphorous acid were added, when mercurous chloride was immediately separated. After the lapse of four hours the mixture was filtered, the precipitate was washed first with concentrated hydrochloric acid in order to re-dissolve bismuth, and then with boiling water in order to re-dissolve any lead chloride which might have been separated out.

The precipitate was oxidised with hydrochloric acid and potassium chlorate, the solution precipitated with hydrogen sulphide, and the precipitate treated with the mixture of potassium sulphide and potassium hydroxide. Small portions remained undissolved. From this filtrate the mercury was precipitated as sulphide by means of ammonium chloride, purified as already described, and weighed.

The filtrate, when subsequently tested with phosphorous acid, gave no further precipitation of mercurous chloride, whence the precipitation must have been complete.

The analyses show that mercury is completely precipitated by phosphorous acid in the simultaneous presence of lead, bismuth, copper, cadmium, arsenic, and antimony. The precipitate, however, always carries down with it slight traces of other metallic compounds (bismuth and lead).

It is established by these investigations that Rose's method permits of a smooth separation of mercury from copper, cadmium, arsenic, and antimony, whether in a nitric or a hydrochloric solution. The separation of mercury ensues smoothly only in a nitric solution, since in a hydrochloric liquid lead chloride is separated out along with the mercurous chloride.

A separation of mercury from bismuth by this method is not practicable in a nitric solution, and in a hydrochloric solution it is not satisfactory, since the mercurous chloride, though completely precipitated, carries down compounds of bismuth. In presence of tin the method is not applicable, since tin tetrachloride has a solvent action upon mercurous chloride and hence prevents the complete precipitation of the mercury.

which it is mixed is well known. And the very purest lithium compounds, when put into a hydrogen flame or a Bunsen burner, show the sodium spectrum more distinctly than it is seen in the ordinary atmosphere.

This difficulty is such that MM. Bunsen, Diehl, and Troost, in their works on lithium, have reached the utmost limit of purity. In my researches on the atomic weight of lithium, I could not exceed their results. Having subsequently found that, under certain atmospheric conditions, a Bunsen burner, or pure hydrogen flame, showed no trace of the sodium spectrum, I reopened my work, and found that there is a method of obtaining a lithium compound which, when put into a non-sodic flame, no longer shows the sodium spectrum at any temperature whatever.

I found that after having made carbonate of lithium, by the method described in the first part of this chapter, so free from all solid bodies, and especially from silica, as not to show the sodium spectrum any more distinctly than it was seen in the air of the laboratory, it sufficed to heat it then in pure air, in an oxyhydrogen blowpipe, with a great excess of hydrogen, in such a manner as to melt it, and reduce it to the state of oxide of lithium. On then raising the lithium compound, in an oxyhydrogen blowpipe, less rich in hydrogen, to a temperature high enough to volatilise, in a few minutes, one-third or one-half of the amount used, according to the relative purity of the carbonate, the spectrum showed no trace of the sodium line. The method depends, therefore, on the simultaneous application of heat and a current of gas.

The complete separation of sodium being a very delicate operation, because it has to be carried out in platinum at a temperature very near the fusing-point of this metal, I must enter into a few details of the method I used to effect this separation and observe the phenomena produced.

I put a concave plate of pure platinum on a strong platinum tripod, to one side of, and the exact height of the slit in, the spectroscope. Having raised this plate to white heat, I put a quantity of carbonate of lithium on it, sufficient to fill the hollow with melted oxide of lithium.

I directed an oxyhydrogen blowpipe flame with an excess of hydrogen, on to the carbonate, by means of a platinum blowpipe, arranged in a suitable position. The mixture of gases and the pressure were previously regulated so as to give a flame 20 c.m. long, and the temperature of the upper third of which should be below that at which hydrogen becomes incandescent, and consequently below the fusing-point of platinum.

When heated, the carbonate melts without altering. If the temperature be then raised, it begins to boil; this lasts until all the carbonic acid is driven off from it. Oxide or hydroxide of lithium made thus is a clear, colourless, very mobile liquid, which wets platinum, and volatilises entirely if the carbonate is quite free from silicates, leaving perfectly pure platinum intact.

During the liberation of carbonic acid, spectrum analysis of either the purple or red flame showed a faint sodium spectrum, which quickly faded away and disappeared entirely, when one-third, or at most a half, of the oxide of lithium was volatilised, and left only the well-known lithium spectrum, the characteristics of which varied in proportion to the temperature and luminosity, as I shall describe further on.

When the sodium has been eliminated from the lithium in perfectly pure platinum dishes, the oxide or hydroxide left is, after cooling, in the form of a colourless, transparent glass, very friable, and soluble in water, forming a perfectly clear solution. The surface of the platinum on which it was purified is exactly the same as it was before the operation. If ordinary platinum be used, containing silicon and foreign metals, especially iron, copper, iridium, and rhodium, the lithium compound is coloured and leaves a residue, when volatilised at a temperature near the fusing-point of platinum. In this case, moreover, the

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 31.)

Spectroscopic Study of Lithium.—Characteristics given to Flames; Electric Spark, Electric Discharge, and Electric Arc by Compounds of Lithium.

The Luminous Spectra of Lithium.—The difficulty in separating a sodium salt from a lithium compound with

surface of the platinum is attacked, and the metal, having been previously treated with dilute hydrochloric acid and washed with water, gives persistent and strong signs of the presence of lithium, when re-melted in an oxyhydrogen blowpipe.

It follows from my observations, made at different times, that the products of the decomposition of carbonate of lithium by oxyhydrogen gas only attack platinum when impurities are present, as is generally the case with commercial platinum.

With oxy-coal-gas the phenomena occur in exactly the same way as with oxyhydrogen.

I return now to the spectrum of lithium under the different conditions in which I observed it. I repeat that my object was at first to find out whether it was possible to form a luminous spectrum of lithium, without seeing the double sodium line at the same time.

I profited by the considerable amount of work I did in order to obtain exceptionally pure carbonate of lithium, when studying afresh the spectrum of this metal. It was, besides, necessary for me to know this spectrum accurately, in order to find out whether it changed under the influence of a great rise of temperature, and under what circumstances this change took place.

If, directly after the oxide of lithium free from sodium solidified it were introduced into the *dark* flame of pure hydrogen, it gave it a very deep purple colour, and on spectrum analysis, a strong red line was seen at from 33 to 34 divisions on my spectroscope, corresponding to from 31.5 to 32.5 on that of M. Bunsen, and a very faint orange line at 45.5 divisions on my spectroscope, corresponding to 45.0 on that of M. Bunsen. This oxide of lithium can be completely volatilised in a long or short hydrogen flame, putting the oxide in front or at the side, without showing a single line. The flame spectrum of chloride of lithium described by M. Bunsen is similar.

On warming this oxide, on the same concave platinum plate on which it was freed from sodium, in the point of an oxy-coal-gas or oxyhydrogen blowpipe, so as to *partially* melt it, this flame also turns very deep purple; spectrum analysis of it shows nothing but a *single* deep red line. On altering the blowpipe, so as to raise the temperature, this line becomes brilliant, and, at the same time, the orange-yellow line mentioned above appears. The temperature may be raised very considerably without any other lines appearing; the only change is that the red and orange-yellow lines become more distinct.

On raising the temperature by the admission of oxygen, so as to bring the excess hydrogen to incandescence, the line originally of a reddish brown appears to become decidedly red, and the orange-yellow line pure yellow; at the same time a pale blue line becomes visible—this line was first noticed by Messrs. Frankland and Lockyer. When working as I have just described, I could never find the line mentioned by M. Lecoq de Boisbaudran, at 135.75 on the micrometer of his spectroscope. If the slit be narrow enough, the spectrum is quite *dark*, marked by the three lines mentioned above.

On raising the temperature to the *fusing-point of platinum*, and introducing into the inner cone of an oxyhydrogen blowpipe flame a small cone of powdered iridium, mixed with oxide of lithium, and attached to a carbon pencil about 1 m.m. diameter, the colour of the inner cone immediately changes to *deep blue*, the envelope of the cone becomes brownish red, and the point of the flame carmine-red. Spectrum analysis of the deep blue and brownish red light shows a very bright continuous spectrum, marked with three lines, amongst which the double sodium line and the second violet line—recently discovered by Messrs. Liveing and Dewar in the spectrum of lithium in the electric arc—are altogether wanting.

On lowering the temperature, the spectral phenomena occur in reverse order. The blue line, which appeared last, disappears first; then the orange-yellow line; and lastly the red line. But the care which I took in carrying on my observations enables me to state that during the

appearances and disappearances of the characteristic lines of oxide of lithium, I was never able to see the sodium line when working on a compound *purified* from sodium. M. Rommelaere, who gave me his earnest assistance in preparing the carbonate of lithium and carrying on these researches, found the same results as I did, when using M. Hilger's fine direct-vision spectroscope, whilst I used in succession the late M. Steinheil's and M. Duboscq's spectroscopes, fitted respectively with two and three prisms.

Sulphate of lithium showed, in a hydrogen flame or in an oxyhydrogen blowpipe, the same spectrum as oxide of lithium under the same conditions; I satisfied myself of this fact when working on sulphates prepared by M. Bunsen and by myself.

During the revision of my spectroscopic work, in collaboration with M. Depaire, we tried to ascertain together—using M. Hilger's spectroscope with two half-prisms and *quartz* eyepiece, instead of the large spectroscope with one prism and *flint* glass eyepiece, and using in succession sulphate of lithium made by M. Bunsen and chloride of lithium made by M. Depaire—whether we could see the second blue line discovered by Messrs. Liveing and Dewar in the spectrum of lithium in the inner cone of an oxy-coal-gas blowpipe.

With this object, we put the lithium compounds successively into an oxy-coal-gas blowpipe made incandescent by an excess of oxygen, and into the inner cone of this flame, by means of a fine carbon pencil which had been cleansed and recently raised to white heat. In spite of all our efforts, *we were not able to detect the second blue lithium line, which was only visible, with the same spectroscope, in the electric spark, discharge, and arc, charged with lithium*, as I shall mention farther on.

Thus there are *three flame spectra* of oxide and sulphate of lithium. The first corresponds to the fusing-point of oxide of lithium—this can be best seen in a Bunsen burner; the second corresponds to the temperature of hydrogen burning in air; and the third to the temperature at which hydrogen becomes incandescent.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 19th, 1895.

MR. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. E. H. Hills, Philip J. Hartog, and Edgar S. Hanes were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. W. H. Barker, 26, Belgrave Road, Longton, Staffs.; Maurice Blood, 15, Clyde Road, Bristol; James Craig, 6, Montague Street, Gt. Western Road, Glasgow; Charles James Femeller Fuller, Mona House, Horwich, Lancs.

Of the following papers those marked * were read:—

*151. "The Liquefaction of Air and Research at Low Temperatures." By JAMES DEWAR, LL.D., F.R.S.

The author reviewed all the forms of apparatus that had been used in low temperature research, pointing out that the best and most economical plant for the production of liquid air or oxygen was one based on the general plan of the apparatus used by Pictet in his celebrated experiments on the liquefaction of oxygen in the year 1878. Instead of using Pictet's combined circuits of liquid sulphur dioxide and carbon dioxide maintained in continuous circulation by means of compression, liquefaction, and subsequent exhaustion, it has been found preferable to select ethylene after Caillietet and Wroblewski, for one

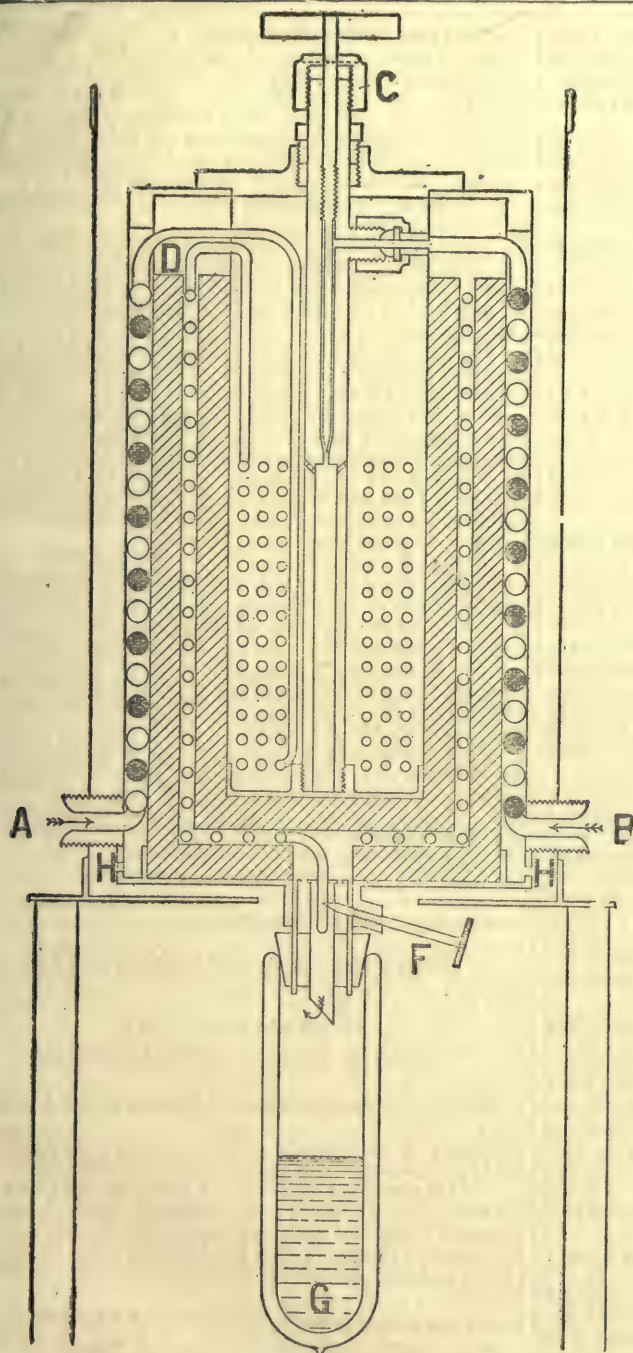


FIG. 1.

A, air or oxygen inlet; B, carbon dioxide inlet; C, carbon dioxide valve; D, regenerator coils; F, air or oxygen expansion valve; G, vacuum vessel with liquid oxygen; H, carbon dioxide and air outlet; O, air coil; ●, carbon dioxide coil.

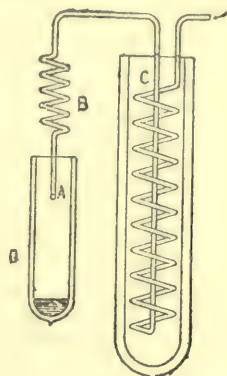


FIG. 2.

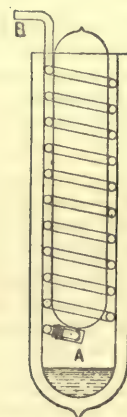


FIG. 3.

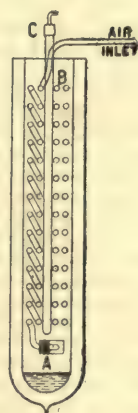


FIG. 4.

circuit, and to join with it either nitrous oxide, or, better, carbon dioxide. Further, instead of making the oxygen to be liquefied by heating potassium chlorate in an iron bomb directly connected with the refrigerator, and thereby

reaching high gas pressures, it has been found more convenient to use gas previously compressed in steel cylinders. The stopcock that Pidet employed to draw off liquid and produce sudden expansion was in his apparatus placed

outside the refrigerator proper, but it is now placed inside, so as to be kept cool by the gases undergoing expansion. This improvement was introduced along with that of isolating the liquid gases by surrounding them with their own vapour in the apparatus made wholly of copper, described and figured in the *Proc. Roy. Inst.* for 1886. In all continuously working circuits of liquid gases used in refrigerating apparatus the regenerative principle applied to cold first introduced by Siemens, in 1857, and subsequently employed in the freezing machines of Kirk, Coleman, Solvay, Linde, and others has been adopted. Quite independently, Professor Kamerlingh Onnes, of Leiden, has used the regenerative principle in the construction of the cooling circuits in his cryogenic laboratory (see paper by Dr. H. Kamerlingh Onnes, on the "Cryogenic Laboratory at Leiden, and on the Production of very Low Temperatures," Amsterdam Akademie, 1894). Apart, therefore, from important mechanical details, and the conduct of the general working, nothing new has been added by any investigator to the principles involved in the construction and use of low temperature apparatus since the year 1878. The *Phil. Mag.* of February, 1895, contains a fantastic claim put forward by Professor Olszewski, of Cracow, that because he used in 1890 a steel tube combined with a stopcock to draw off liquid oxygen, he had taught the world, to use his own language, "the method of getting large quantities of liquid gases." But when, in addition, Olszewski alleges, four years after the event, that the experiments made at the Royal Institution since 1891 are chiefly borrowed from Cracow, and that he is entitled to the credit of all low temperature research subsequent to 1891, because of his steel tube and stopcock invention, one can only wonder at the meagre additions to knowledge that in our time are unhesitatingly brought forward as original, and more especially that scientific men could be got to give them any currency in this country. Such persons should read the late Professor Wroblewski's pamphlet entitled "Comment l'air a été Liquefié" (Paris, Librairie du Luxembourg, 1885), and make themselves generally acquainted with his work before coming to hasty conclusions on claims of priority brought forward by the Professor of Chemistry at Cracow.

Liquefying Apparatus.—The author proceeded to describe the construction and show the working of a laboratory apparatus for the production of liquid oxygen and other gases, represented in section (Fig. 1). With this simple arrangement 100 c.c. of liquid oxygen can readily be obtained, the cooling agent being carbon dioxide, at the temperature of -79° , no exhaustion being used. The gaseous oxygen, cooled before expansion by passing through a spiral of copper tube immersed in solid carbon dioxide, passes through a fine screw stopcock under a pressure of 100 atmos., and thence backwards over the coils of pipe. The liquid oxygen begins to drop in about a quarter of an hour from starting. The general arrangement of the circuits will be easily understood from the sectional drawing. The pressure in the oxygen cylinders at starting is generally about 150 atmos., and the best results are got by working down to about 100°. This little apparatus will enable liquid oxygen to be used for demonstration and research in all laboratories.

Vacuum Vessels.—It has been shown in previous papers* that a good exhaustion reduces the influx of heat to one-fifth part of what is conveyed when the annular space in such double-walled vacuum vessels is filled with air. If the interior walls are silvered, or excess of mercury is left in the vessel, the influx of heat is diminished to one-sixth part of the amount entering without the metallic coating. The total effect of the high vacuum and silvering is to reduce the ingoing heat to 1/30th part, or, roughly, 3½ per cent. Vessels constructed with three dry air spaces only reduced the influx of heat to 35 per cent. An ordinary mercury vacuum vessel is therefore ten times more

economical for storing liquid air, apart from considerations of manipulation, than a triple annular-spaced air vessel. It has been suggested that the metallic coating of mercury does no good, because Pictet has found that all kinds of matter at low temperatures become transparent to heat. The results above mentioned dispose of this assumption, and direct experiment proves that no increase in the transparency of glass to thermal radiation takes place by cooling to the boiling-point of air.*

Solid Air.—As Professor Olszewski has recently alleged that air does not solidify at the lowest pressures (*Phil. Mag.*, February, 1895), the author's former experiments were repeated on a larger scale. If a litre of liquid air is placed in a globular silvered vacuum vessel and subjected to exhaustion, as much as half a litre of solid air can be obtained and maintained in this condition for half an hour. At first the solid is a stiff, transparent jelly, which, when examined in the magnetic field, has the liquid oxygen drawn out of it to the poles. This proves that solid air is a nitrogen-jelly containing liquid oxygen. Solid air can only be examined in a vacuum or in an atmosphere of hydrogen, because it instantly melts on exposure to the air, giving rise to the liquefaction of an additional quantity of air. It is strange to see a mass of solid air melting in contact with the atmosphere, and all the time welling up like a kind of fountain.

Samples of Air Liquefied in Sealed Flasks.—In a previous paper "On the Relative Behaviour of Chemically Prepared and of Atmospheric Nitrogen" (*Proc. Chem. Soc.*, December, 1894) the plan of manipulating such samples was described. Two flasks of dry air that had stood over phosphoric anhydride were liquefied side by side, the only difference between the samples being that one was free from carbonic acid. The one gave a liquid that was perfectly clear, the other was turbid from the 0.04 per cent of carbon dioxide. The temperature was now lowered by further exhaustion of the liquid air surrounding the tubes until both liquids became solid. The flasks were then sealed off for the purpose of examining the composition of the air that had not been condensed. The one sample contained oxygen, 21.19 per cent, and the other 20.7 per cent. This is an additional proof to the one previously given, that, substantially, the oxygen and nitrogen in air liquefy simultaneously, even under gradually diminishing pressure, and that in these experiments all the known constituents of air are condensed together. These results finally disproved the view expressed in "A System of Inorganic Chemistry" 1891, p. 70), by Professor Ramsay, where he says: "Air has been liquefied by cooling to -192° , but as oxygen and nitrogen have not the same boiling-points, the less volatile oxygen doubtless liquefies first." In the author's former experiments, the substance now known as argon, became solid before nitrogen, but chemical nitrogen and air nitrogen, with its 0.1 per cent of argon, behaved in substantially the same way on liquefaction.

Liquid Nitric Oxide.—Great interest attaches to the behaviour of nitric oxide at low temperatures. Professor Olszewski has examined the liquid and describes it as colourless. Dr. Scott has prepared in different ways samples of nitric oxide. These have been transferred to liquefaction flasks, where they were left in contact with potash, sulphuric acid, or phosphoric acid for many days before use. Each of the samples, when cooled, gave a nearly white solid, melting into a blue liquid. The colour is more marked at the melting-point than at the boiling-point. Liquid nitric oxide is not magnetic; neither is the solid phosphorescent. Colour in the oxides

* "On Liquid Atmospheric Air," *Proc. Roy. Inst.*, 1893; "Scientific Uses of Liquid Air," *Ibid.*, 1894.

* As this is passing through the press, I observe that M. Caillaud, at the last meeting of the French Academy (*Comptes Rendus*), presented a paper by M. Solvay of Brussels, in which my device of vacuum vessels is attributed to M. Caillaud, and tacitly accepted by him! In 1873 I had already used a highly exhausted vessel of similar shape to the vacuum test-tube, in calorimetric experiments. See paper on "The Physical Constants of Hydrogenium," *Trans. Roy. Soc. Ed.*, vol. xxvii.

of nitrogen evidently begins with the second oxide. Solid nitric oxide does not show any chemical action in liquid oxygen, provided the tube containing it is completely immersed; but if the tube full of liquid oxygen is lifted into the air, almost instantly a violent explosion takes place.

Specific Gravities taken in Liquid Oxygen.—In a good vacuum vessel specific gravities may be taken in liquid oxygen with as great ease as in water.

Some twenty substances were weighed in liquid oxygen, and the apparent relative density of the oxygen determined. The results were then corrected, using Fizeau's values for the variation of the coefficient of expansion of the solids employed, and thereby the real density of liquid oxygen calculated. The resulting value was 1.1375, bar. 766.5, in the case of such different substances as cadmium, silver, lead, copper, silver iodide, calc-spar, rock crystal. Direct determinations with an exhausted glass cylindrical vessel displacing about 22 c.c. gave 1.1378. Fizeau's parabolic law for the variation of the coefficient of expansion holds down to -183° . The solid which showed the greatest contraction was a block of compressed iodine, the one that contracted least being a compressed cylinder of silver iodide. Wroblewski gave the density of liquid oxygen at the boiling-point as 1.168, whereas Olszewski found 1.124. The variation of density is about ± 0.0012 , for 20 m.m. barometric pressure. Much work requires to be done in the accurate determination of the physical constants of liquid gases.

Liquid Air.—A large silver ball weighed in liquid air gave the density of the latter as 0.910, and the corresponding density of nitrogen at its boiling-point 0.850. It is difficult to be quite certain that the constituents of liquid air are in the same proportion as the gaseous ones, so that further experiments must be made. Liquid air kept in a silvered vacuum vessel gradually rises in boiling-point from the instant of its collection, the rate of increase during the first hour being nearly directly proportional to the time. As the increase amounted to 1° in ten minutes the boiling-point of oxygen ought to have been reached within two hours. The density of liquid air, however, does not reach that of pure oxygen even after thirty hours' storage. The large apparatus can be arranged to deliver liquid air containing 49 per cent of oxygen, which gives off gas containing 20 per cent of oxygen, rising after six hours to 72.6 per cent.

Combustion in Liquid Oxygen.—A small ignited jet of hydrogen burns continuously below the surface of liquid oxygen, all the water produced being carried away as snow. There is a considerable amount of ozone formed, which concentrates as the liquid oxygen evaporates. In the same way graphite or diamond, when properly ignited, burns continuously on the surface of liquid oxygen, producing solid carbonic acid and generating ozone. If liquid oxygen is absorbed in wood charcoal, or cotton wool, and a part of the body heated to redness, combustion can start with explosive violence.

Gas Jets containing Liquid.—The experiments of Joule and Thomson and Regnault on the temperature of gas jets issuing under low pressures are well known. The following observations refer to the pressure required to produce a lowering of temperature sufficient to yield liquid in the gas jet.

The apparatus used in the study of highly compressed gas jets is represented in Fig. 2; where c is a vacuum tube which holds a coil of pipe about 5 m.m. in diameter along with carbon dioxide or liquid air for cooling the gas before expansion, and A is a small hole in the silver or copper tube about $\frac{1}{2}$ m.m. in diameter, which takes the place of a stopcock. When carbon dioxide gas at a pressure of 30 or 40 atmos. is expanded through such an aperture, liquid can be seen where the jet impinges on the wall of the vacuum tube along with a considerable amount of solid. If oxygen gas escapes from the small hole at the pressure of 100 atmos., having been cooled previously to -79° in the vessel c, a liquid jet is just visible. It is interesting to note in passing that Pictet could get no

liquid oxygen jet below 270 atmos. This was due to his stopcock being massive and outside the refrigerator. If the oxygen is replaced by air no liquid jet can be seen unless the pressure is raised to 180 atmos. If the carbon dioxide is cooled by exhaustion (to about 1 m.m. pressure) or -115 , then liquid air can easily be collected in the small vacuum vessel D, or if the air pressure is raised above 200 atmos., keeping the cooling at -79° as before. The chief difficulty is in collecting the liquid owing to the rapid current of gas. The amount of liquid in the gas jet is small and its collection is greatly facilitated by directing the spray on a part of the metallic tube above the little hole or by increasing resistance to the escaping gas by placing some few turns of the tube, like B in the figure, in the upper portion of the vacuum tube, or generally by pushing in more tube in any form. A vacuum vessel shaped like an egg-glass also works well. This practically economises the cool gas which is escaping to reduce the temperature of the gas before expansion, or, in other words, it is the cold regenerative principle. Coleman pointed out long ago that his air machine could be adapted to deliver air at as low a temperature as has yet been produced in physical research. Both Solvay and Linde have taken patents for the production of liquid air by the application of cold regeneration, but the latter has the credit of having succeeded in constructing an industrial apparatus (the plans of which are not yet published) that is lowered in temperature to -140° , or to the critical point of air in about fifteen hours, and from which liquid air containing 70 per cent oxygen is collected after that time.

For better isolation, the pipe can be rolled between two vacuum tubes, the outer one being about 9 inches long and $1\frac{1}{2}$ inch diameter, as shown in Fig. 3. The aperture in the metal pipe has a little piece of glass tube over it which helps the collection of the liquid. With such a simple apparatus and an air supply of 200 atmos. with no previous cooling, liquid air begins to collect in about five minutes, but the liquid jet can be seen in between two and three minutes. It is not advisable to work below 100 atmospheres.

In Fig. 4 the metallic tube in the vacuum vessel is placed in horizontal rings, leaving a central tube to allow the glass tube c to pass, which is used to cool bodies or examine gases under compression. The inner tube can be filled for an inch with liquid air under a pressure of 60 atmos. in about three minutes. Generally, in the experiments, about $\frac{1}{2}$ to 4 cubic feet of air passes through the different sized needle holes per minute when the pressure is about 200 atmos. As the small hole is apt to get stopped, for general working it is better to use a needle stopcock, worked from the outside by a screw passing through the middle of the coil of pipe. A double coil of pipe has advantages in the conduct of some experiments. The efficiency is small, not exceeding the liquefaction of 2 to 5 per cent of the air passing, but it is a quick method of reaching low temperatures and easy to use for cooling tubes and collecting a few hundred c.c. of liquid air, especially if the compressed air is delivered at the temperature of -79° before expansion. With larger vacuum vessels and larger regenerating coils, no doubt the yield of liquid could be increased. The liquid air resulting from the use of this form of apparatus contains about 50 per cent of oxygen. If the air is cooled with solid carbonic acid previous to its reaching the vacuum tube coil of pipe, the only change is to reduce the percentage of oxygen to 40. Successive samples of liquid taken during the working had nearly the same composition. If the arrangement shown in Fig. 2 is used, with silver tube, about $\frac{1}{16}$ in. bore, and a foot or two coiled in upper part of the vacuum vessel, liquid air containing 25 per cent of oxygen was obtained. On the other hand, the percentage of oxygen can be increased by a slight change in the mode of working.

In the above experiments air is taken at the ordinary temperature, which is a little above twice its critical tem-

perature, and is partially transformed in a period of time which, in my experiments, has never exceeded ten minutes, simply and expeditiously into the liquid state at its boiling-point, -194° , or a fall of more than 200° has been effected in this short period of time.

Experiments on Hydrogen.—Wroblewski made the first conclusive experiments on the liquefaction of hydrogen in January, 1884. He found that the gas cooled in a tube to the boiling-point of oxygen, and expanded quickly from 100 to 1 atmos., showed the same appearance of sudden ebullition as Cailletet had seen in his early oxygen experiments. No sooner had the announcement been made than Olszewski confirmed the result by expanding hydrogen from 190 atmos., previously cooled with oxygen and nitrogen in a vacuum. Olszewski declared in 1884 that he saw colourless drops, and by partial expansion to 40 atmos. the liquid hydrogen was seen by him running down the tube. Wroblewski could not confirm these results, his hydrogen being always what he called a "liquide dynamique." He proposed to get "static" liquid hydrogen by the use of hydrogen gas as a cooling agent. From this time until his death, in the year 1888, Wroblewski devoted his time to a laborious research on the isothermals of hydrogen at low temperatures. The data thus arrived at enabled him, by the use of Van der Waal's formulæ, to define the critical constants of hydrogen, its boiling-point, density, &c., and the subsequent experiments of Olszewski have confirmed the accuracy of the results. In a paper published in the *Phil. Mag.*, September, 1884, "On the Liquefaction of Oxygen and the Critical Volumes of Fluids," the suggestion was made that the critical pressure of hydrogen was wrong, and that instead of being 99 atmos. (as deduced by Sarrau from Amagat's isothermals) the gas had probably an abnormally low value for this constant. This view was substantially confirmed by Wroblewski finding a critical pressure of $13\frac{1}{3}$ atmos., or about one-fourth that of oxygen. The *CHEMICAL NEWS* (September 7, 1894) contains an account of the stage the author's hydrogen experiments had reached at that date. The object was to collect liquid hydrogen at its boiling-point, in an open vacuum vessel, which is a much more difficult problem than seeing the liquid in a glass tube under pressure and at a higher temperature. In order to raise the critical point of hydrogen to about -200° from 2 to 5 per cent of nitrogen or air was mixed with it. This is simply making an artificial gas containing a large proportion of hydrogen, which is capable of liquefaction by the use of liquid air. The results are summed up in the following extract from the paper:—"One thing can, however, be proved by the use of the gaseous mixture of hydrogen and nitrogen, viz., that by subjecting it to a high compression at a temperature of -200° and expanding the resulting liquid into air, a much lower temperature than anything that has been recorded up to the present time can be reached. This is proved by the fact that such a mixed gas gives, under the conditions, a paste or jelly of solid nitrogen, evidently giving off hydrogen because the gas coming off burns fiercely. Even when hydrogen containing only some 2 to 5 per cent of air is similarly treated the result is a white solid matter (solid air) along with a clear liquid of low density, which is so exceedingly volatile that no known device for collecting has been successful."

In Professor Olszewski's paper "On the Liquefaction of Gas" (*Phil. Mag.*, 1895), after detailing the results of his hydrogen experiments, he says: "The reason for which it has not hitherto been possible to liquefy hydrogen in a static state, is that there exists no gas having a density between that of hydrogen and nitrogen, and which might be, for instance, 7–10 ($H=1$). Such a gas would be liquefied by means of liquid oxygen or air as cooling agent, and afterwards used as a recognised menstruum in the liquefaction of hydrogen." Science will probably have to wait a very long time before this suggestion of how to get "static" liquid hydrogen is realised. The proposal Wroblewski made in 1884 of using the expansion of hy-

drogen as a cooling agent to effect the change of state is far more direct and practicable.

Liquid Hydrogen Jet and Solid Oxygen.—Hydrogen, cooled to -194° (80° abs. $t.$) the boiling-point of air, is still at a temperature which is two and a half times its critical temperature, and its direct liquefaction at this point would be comparable to that of air taken at 60° , and liquefied by the apparatus just described. Now, air supplied at such a high temperature greatly increases the difficulty and the time required for liquefaction. Still, it can be done, even with the air supply at 100° , in the course of seven minutes, and this is the best proof that hydrogen, if placed under really analogous conditions, at -194° must also liquefy with the same form of apparatus. Hydrogen, cooled to -200° , was forced through a fine nozzle under 140 atmos. pressure, and yet no liquid jet could be seen. If the hydrogen contained a few per cent of oxygen the gas jet was visible, and the liquid collected, which was chiefly oxygen, contained hydrogen in solution, the gas given off for some time being explosive.

If, however, hydrogen, previously cooled by a bath of boiling air, is allowed to expand at 200 atmos. over a regenerative coil similar to that shown in Fig. 2, but longer, a liquid jet can be seen after the circulation has continued for a few minutes along with a liquid which is in rapid rotation in the lower part of the vacuum vessel. The liquid did not accumulate, owing to its low specific gravity and the rapid current of gas. These difficulties will doubtless be overcome by the use of a differently shaped vacuum vessel and by better isolation. The liquid jet can, however, be used as a cooling agent like the spray of liquid air obtained under similar circumstances, and, this being practicable, the only difficulty is one of expense. In order to test, in the first instance, what the hydrogen jet could do in the production of lower temperatures, liquid air and oxygen were placed in the lower part of the vacuum tube just covering the jet. The result was that in a few minutes about 50 c.c. of the respective liquids were transformed into hard white solids resembling avalanche snow, quite different in appearance from the jelly-like mass of solid air got by the use of the air-pump. The solid oxygen had a pale bluish colour, showing by reflection all the absorption-bands of the liquid. The temperatures reached, and other matters, will be dealt with in a separate communication. There is no reason why a spray of liquid hydrogen, at its boiling-point in an open vacuum vessel, should not be used as a cooling agent in order to study the properties of matter at some 20° or 30° above the absolute zero. The sole difficulty is the cost.

Fluorine.—This is the only widely-distributed element that has not been liquefied. Some years ago Wallach and Hensler pointed out that an examination of the boiling-points of substituted halogen organic compounds led to the conclusion that, although the atomic weight of fluorine is 19 times that of hydrogen, yet it must in the free state approach hydrogen in volatility. This view is confirmed by the specific refractive index which Gladstone showed was rather lower than hydrogen. If the chemical energy of fluorine at low temperatures is abolished like that of other active substances, then some kind of glass or other transparent material not so brittle as calcium fluoride could be employed in the form of a tube, and its liquefaction achieved by the use of hydrogen as a cooling agent.

During the conduct of these investigations, able assistance has been rendered by Mr. Robert Lennox, whose name has been so often mentioned in the Royal Institution lectures. Valuable help has also been given by Mr. J. W. Heath, Assistant at the Royal Institution.

DISCUSSION.

Professor RAMSAY remarked that Professor Olszewski had succeeded in liquefying hydrogen, and from unpublished information received from Cracow, he was able to state that a fair amount of liquid had been obtained, not

as a froth, but in a state of quiet ebullition, by surrounding a tube containing compressed hydrogen by another tube also containing compressed hydrogen at the temperature of oxygen boiling at a very low pressure. On allowing the hydrogen in the middle jacket suddenly to expand, the hydrogen in the innermost tube liquefied, and was seen to have a meniscus. Its critical point and its boiling-point, under atmospheric pressure, were determined by means of a resistance thermometer. There would appear to be no difficulty in distinguishing the meniscus of hydrogen, where the liquid is 50 times as heavy as the gas, for it is perfectly easy to see a meniscus with such a liquid as ether, at temperatures so near the critical point that the liquid has only three or four times the density of the gas.

Mr. BLOUNT said that the first account of the Linde process for liquefying air had been published in the early autumn of 1895, in the form of a paper read by Herr Schröter before the Association of German Engineers at Aachen. Briefly, it consisted in taking advantage of the fact that air, not being a perfect gas, is permanently cooled when allowed to expand through a narrow opening without doing external work. The lowering of temperature was expressed by Joule and Thomson's formula,—

$$t = \frac{p_2 - p_1}{4} \left(\frac{289}{T_1} \right)$$

where t is the fall in temperature in degrees centigrade, p_2 is the pressure of the air before it passes the opening, p_1 is the pressure of the air after passing the opening, and T_1 is the absolute temperature of the air before passing the opening. The effect was made cumulative by causing the air thus cooled to cool that which was about to pass through the opening. This was effected by the use of two long concentric tubes, the inner conveying the air to be cooled, and the annular space between the two being traversed by the cooling air. Circulation was maintained by means of an ordinary air compressor, and the temperature fell until the critical temperature was reached. A subsidiary compressor supplied fresh air to the cycle to replace that liquefied. The process was interesting because it differed fundamentally from those usually employed for the liquefaction of difficultly condensable gases, in two respects, viz. (1) it dispensed with the use of intermediate cooling agents, and (2) it applied a method for the cumulative withdrawal of heat analogous to the converse process of heat regeneration. Trials of the process had been made on a considerable scale, and there appeared to be no difficulty in liquefying air cheaply and in quantity.

Lord PLAYFAIR said, as a Past-President of the Society he was aware that it is not the practice to move a vote of thanks to the reader of a paper, so that he must not conclude with a motion to that effect. But he was sure that he was expressing the sentiments of all present, when he said that they were grateful for the admirable exposition and splendid experiments which they had heard and seen. It is known to them all that an undesirable controversy had been going on as to how much originality there is in the researches of Professor Dewar, whom he had the honour of claiming as an old student and assistant when he was Professor in Edinburgh. He had wasted his time in reading these attacks, and they have had no influence on his mind, or rather that they had influenced him to send a subscription to the Royal Institution towards the cost of the apparatus. The diagram of Piçet's apparatus, now shown, certainly gives to the general chemist the most original conceptions as to how the problem of liquefying gases should be attacked. But if Piçet were now with them, and could see the great advances which had been made on his ideas, he would be the first to recognise their importance, and to congratulate Professor Dewar. It is only in mythology that Minerva, full grown, and panoplied in complete armour, is born from the brain of Jupiter after a prolonged gestation. In human

brains one discovery suggests another, and we proceed to the goal of knowledge step by step. The world now feels that Watt's discoveries, in improving the steam-engine, gave an enormous impulse to civilisation. But the men of his day were petty enough to deny him merit, and they went to a court of justice to prove that every one of his discoveries had previously been made by other men, and, more strange still, the court agreed with them and solemnly declared that Watt had done nothing to improve the steam-engine. Every discovery can be connected with previous discoveries. Would the merit of Rayleigh and Ramsay be lessened as the discoverers of argon because Cavendish had it undoubtedly as the residue in his tube in his famous experiment on air? It is to be hoped that Professor Dewar will go on with his magnificent experiments on the liquefaction of gases, and with the researches which come from them, without caring for the mosquitoes of science which buzz about his ears.

Dr. ARMSTRONG said that, after what had fallen from Lord Playfair, he would venture to express the opinion that the attacks made on Professor Dewar during the past few months were disgraceful. In these days we should encourage as far as possible all who were engaged in such dangerous and difficult work, not decry their labours. The history of the Royal Institution in the past, in so far as concerned the liquefaction of gases, was a glorious one, and he had no doubt that when the work done there more recently came to be considered without prejudice, it would be regarded as equally important. In fact there was evidence of this already. Professor Onnes, of Leiden, who, with most limited appliances and means, had already accomplished so much in the field of research at low temperatures,—an acknowledged expert in these matters,—in a recent publication, in which justice was done to all workers, clearly recognised that much credit was due to Professor Dewar for his various improvements. He did not consider it necessary to thank Professor Dewar, but thought that his assistants should not be forgotten. Messrs. Lennox and Heath had done much service in connection with the work generally, and especially in making the present demonstration possible.

Professor DEWAR, in reply, stated that he could have no knowledge of unpublished work on the liquefaction of hydrogen. The mere fact of liquefaction was first definitely given by Wroblewski, although Cailletet had made an earlier experiment of the same kind. His paper contained a quotation from Prof. Olszewski's communication made to the *Philosophical Magazine* in Feb., 1895, in which Olszewski distinctly says that he had not succeeded in getting liquid hydrogen in the "static" condition. Further, in a later paper, published in the same journal, for August, 1895, no mention is made of getting a "fair amount of liquid in a state of quiet ebullition" or of seeing a "meniscus." Even the method of working, to which reference has been made, is not mentioned, far less the result of the experiments made by the speaker in 1894. He was unable to understand why such a point should be made of seeing a meniscus, considering that the liquid can be seen. The remarks about the difficulty of separating liquid hydrogen from the gas had reference to a fine rain of fluid in a rapidly rushing stream of gas passing through vacuum vessels, and has no relation whatever to critical point phenomena to which reference had been made. If the liquid oxygen and air-jets shown have any resemblance to the Linde apparatus described by Mr. Blount, chemists, for once, may be congratulated that a small laboratory apparatus works in some respects better than a large industrial plant. The Linde apparatus after working fifteen hours is capable of reducing the temperature of air to its critical point, whereas in the present small apparatus liquid air is produced in five minutes. Such a process cannot replace the use of "cooling agents" when considerable quantities of liquid air have to be produced in a short period of time as in ordinary laboratory work. It is a mistake to attribute to

Linde the idea of using the "cumulative withdrawal of heat," for the first time, in his apparatus; but he has succeeded in making a workable industrial machine, and that is a very important step. The late Professor Wroblewski, as early as the year 1884, predicted that liquid air would be the refrigerating agent of the future; his prophecy seems about to be realised.

(To be continued).

NOTICES OF BOOKS.

L'Eau Potable. ("Potable Water"). By FRANÇOIS COREIL. Paris: J. B. Baillière et Fils. 1896. 16mo., pp. 359.

THE present volume is one of the series of important works issued by Messrs. J. B. Baillière and Son under the general title "Encyclopédie de Chemie Industrielle." It may justly take a very high rank among the hygienic writings of the day.

After an Introduction, in which the author recognises that water is still the true king of non-intoxicating beverages, M. Coreil treats of its elements, normal and accidental or injurious. On the effects of waters rich in mineral impurities we find no certain decision. The statistics collected by Letheby, who finds that in sixty-five British towns these mineral matters are found in proportions inversely as the death-rates, are vitiated by the fact that the cities supplied with pure water—such as Glasgow, Manchester, Leeds, Sheffield, &c.—are precisely those which suffer from over-crowding, unhealthy occupations, and polluted atmospheres. As regards organic pollutions, the author insists that a water cannot produce any given malady unless it has received the pathogenic germs of such malady.

A quotation shows that even Hippocrates was fully aware of the sanitary or anti-sanitary influence of the water-supply, and of its correction. Nevertheless it is still a debated question whether diseases are more due to the water actually drank or to that stagnating below the soil (*Trink-wasser* and *Grund-wasser* theories of German hygienists). In a passage here quoted, from a German engineer of the name of Grahn, it is asserted that so long as Birmingham was supplied with the dirty water of the Thames (*sic!*) it was one of the healthiest of large cities, but since it has begun to consume the pure water from the springs of the red sandstone its mortality has been increasing daily. On the contrary, observations made in France lead to more intelligible results, and are more in conformity with what might be expected.

In a very interesting chapter M. Coreil examines the influence of impure waters in a number of diseases—goitre, dysentery, calcular affections, malaria, jaundice, typhoid fever, and especially cholera.

The presence of animal parasites—such as the *Medina* worm, the larvæ of *Bilharzia hematobia*, and the earlier stages of tapeworm—are also traced to the use of impure waters. The author has omitted to mention that the occurrence of hydatidous cysts is due to water polluted by the excretions and secretions of dogs, which are the "intermediate hosts" of some species of tænia.

In treating of the sources of drinking-water,—such as rain, snow, springs, rivers, wells, &c.,—the author shows very clearly how the water of a stream becomes gradually polluted as it traverses a populous and cultivated region. One error seems to have escaped him: he mentions (p. 46) that the higher vegetation (such as water-cress and reeds) gradually give place to Algae and bacteria. Now Slater has shown by experiment that water-cress flourishes most luxuriantly in foul, unpurified sewage. M. Coreil admits the self-purification of rivers as a fact, but he omits to mention, among the agencies of this improvement, the nascent oxygen given off from the leaves of aquatic vegetation.

The second part of the work is devoted to the chemical analysis of waters, including the taking of samples. The official questions which must be replied to by any community about to introduce a new water-supply are exceedingly judicious, and might well be adopted in Britain.

Then follow the methods for chemical analysis, qualitative and quantitative.

For the recognition of nitrates we find described the brucine and diphenylamine processes, and that with sulphuric acid and phenol. The methods recommended for the detection of nitrites are those of Schœnbein, Trommsdorff, and Griess. For determining albumenoid ammonia we find the method known as that of Wanklyn and Chapman.

Our space unfortunately does not allow us to abstract the instructions given for the microscopic and microbiological examination of waters. It must suffice for us to say that the directions given are most elaborate, and are accompanied with a description of the principal morbid species.

This work should be added to the library of every hygienic chemist.

A Manual of Inorganic Chemistry. By T. E. THORPE, B.Sc., Ph.D., Sc.D., LL.D., F.R.S. London and Glasgow: Collins, Sons, and Co. (Ltd.) 1896. Vol. I. The Non-Metals, pp. 511. Vol. II.—The Metals, pp. 430.

AS regards extent this work occupies a useful medium position between such bulky and necessarily expensive works as those of L. Gmelin, Roscoe, and Schorlemmer, and a few others of similar rank, and the meagre handbooks written in accordance with some "syllabus."

Dr. Thorpe has brought down his subject to the level of the most recent discoveries. We have a full account of argon as at present ascertained. Helium figures as a Supplement to Vol. I. The less-known elements, such as the metals of the rare earths, and gallium and germanium, are carefully described. Spectral analysis and electro-chemical decomposition form the subject of a chapter in the second volume. Fluorine is frankly placed at the head of the halogens. Hydrazine and its compounds, and cyanogen, are included in the inorganic part of the Science.

The present number of the elements is given a 75 to 80. They are distinctly regarded as provisional, though the author indulges in no speculations concerning their origin or any previous or future state of matter. The Periodic Law figures in the first chapter of Vol. II.

This work must be recommended for senior students. They will find here no important class of phenomena ignored, and they will not learn from the author anything which they will need to unlearn in their after career. Dr. Thorpe's work is also of no small merit as a work of reference.

The Chemistry of Pottery. By KARL LANGENBECK, Superintendent of the Mosaic Tile Company, formerly Superintendent of Rookwood Pottery, Chemist to the American Encaustic Tiling Co., &c. Eastern Pennsylvania: Chemical Publishing Co. 1895. Pp. 197.

WE can scarcely admit the assertion conveyed in the author's Preface, viz., "that the pottery industries of England have afforded chemists little opportunity for systematic work, so that they have remained largely on an empirical basis, and have supplied nothing of moment to chemical technology." We have lived under the impression that systematic experimental work had been a main feature in the establishments of Wedgwood in the past and of Doulton in the present. The work before us can scarcely be regarded as written in idiomatic English. "Unlocking" clays or other minerals is an expression apt to puzzle readers who are not German scholars.

The art of sampling the raw materials, and the ne-

cessity for its correct performance, have been painfully brought under the notice of every chemist who has had to analyse specimens not fairly characteristic of the bulk which they profess to represent. The regulation of temperatures by means of Seger's pyrometric cones will doubtless have found almost universal adoption.

The author is justifiably severe upon receipts founded on analyses which, if carefully and accurately executed, take no account of the temperatures to be employed.

As regards glazes, Mr. Langenbeck seems to give a preference to those containing lead. That they are very widely employed—indeed to a predominating degree—must be admitted; but they are so generally, strongly, and justly objected to on hygienic grounds, that one of the chief duties of the ceramic chemist should be their suppression by some safe composition.

The work before us, though of course written with a predominating regard to American materials, will be of use to British ceramic industrialists.

CORRESPONDENCE.

ESTIMATION OF INSOLUBLE PHOSPHATE.

To the Editor of the *Chemical News*.

SIR,—With reference to a "Note on the Rapid Estimation of Insoluble Phosphate," by Mr. Vincent Edwards (*CHEMICAL NEWS*, vol. lxxiii., p. 25), I do not think that the process would work out with a very great degree of accuracy, for the following reasons:—

When the solution of "insoluble phosphate" in HCl is neutralised and made alkaline with ammonia, and the acetic acid added, a certain proportion of the phosphoric acid would be precipitated in combination with the iron and alumina present. The phosphates of iron and alumina so precipitated are not of constant composition, containing varying quantities or percentages of phosphoric acid. Freshly precipitated phosphates of iron and alumina are only partially acted upon by standard solutions of uranium acetate or nitrate, and even when so acted upon they behave in a very inconstant manner.

Under these circumstances, this proposed volumetric process would give very uncertain results, and could hardly compete with the old gravimetric process except for very rough results. The following is the best method of which the writer is aware for the rapid estimation of the insoluble phosphate in "supers" and other dissolved manures, which, though not strictly accurate, gives results very near to the truth, quite sufficiently so for most work's laboratories. The process is, of course, quite old and well known, but perhaps there may be no harm in reproducing it here:—

Weigh 1 or 2 grms. of the substance to be examined; wash out the soluble phosphate in usual way, with first cold and then hot water; collect the insoluble residue on a filter, and wash with hot water; transfer the residue from the filter back into the beaker, add strong HCl, digest on sand-bath until all the phosphate has dissolved, add a small quantity of hot water; filter off the sand and insoluble matters, wash with hot water, put the filtrate on sand-bath and raise to boiling; add strong ammonia in excess. Filter off the precipitate, wash twice with hot water, stirring up the precipitate each time with the jet; dissolve the precipitate off the filter-paper back into the beaker with dilute HCl (1 in 4). Raise to boiling again, add strong ammonia in excess, filter off, dry, burn, and weigh as the insoluble phosphate.

The amount of substance advised to be taken by Mr. Edwards for his process appears to me to be rather small for an estimation of this kind, and might prove another source of error.—I am, &c.,

GEO. H. ALLIBON.

Messrs. Richardson Bros. and Co.,
Manure Works, Belfast, January 22, 1896.

IS ARGON AS IDLE AS ITS NAME SUGGESTS.

To the Editor of the *Chemical News*.

SIR,—I should like to suggest to the authors of argon, Lord Rayleigh and Prof. W. Ramsay, who have all the appliances for its production, to ascertain whether the new gas has any action towards fermentation, either in retarding or facilitating it, and what effect has it in general.

Also what is the behaviour in the preservation of foods, such as milk, &c.

And its physiological action on bacteria.—Yours truly,
P. L. ASLANOGLOU.

January 13th, 1896.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 27, December 30, 1895.

Acoustic Analysis of Mixtures of two Gases of different Densities.—E. Hardy.—The author attaches a microphone to each of two sonorous pipes. An electric current traverses them in succession, and then passes into an ordinary telephonic recipient placed at some distance. This recipient repeats distinctly either the pure sound or the beats produced by the sonorous pipes. With mixtures of air and coal-gas the author obtained:—For 1/1000th part of gas, 2 to 3 beats in twenty seconds; for 2/1000th part, about 6 beats in the same time; and for 20/1000th, 60 beats in the same time.

Spectral Displacement of the Solar Thermic Maximum.—M. Aymonnet.—The author gives his results in the form of tables, and concludes with the observation that the more crown glass is contained in the spectroscopic the further the maximum is displaced towards the violet.

Combustion of Acetylene.—H. Le Chatelier.—Mixtures of acetylene with air containing a proportion of the gas below 7.74 per cent burn, yielding carbonic acid and water, with a yellowish flame feebly luminous. For proportions of acetylene between 7.74 and 17.37 per cent, the flame is of a pale blue with a slight yellowish halo. The products of the combustion are carbon dioxide, carbon monoxide, watery vapour, and hydrogen. If acetylene is burnt with an equal volume of oxygen it gives a temperature of 4000°; consequently superior by 1000° to the mixture of oxygen and hydrogen. The products of combustion consist exclusively of carbon monoxide and hydrogen, both reductive gases. This double property will render the use of acetylene in laboratories very valuable, either in the gas blowpipe for the production of high temperatures, or in ordinary air burners for spectrum analysis.

Fixation of Nitrogen by the Alkaline-earth Metals.—L. Maquenne.—In the course of my researches on the alkaline-earth metals, I have called attention to two novel and curious properties of these substances, i.e., their power of forming directly definite compounds with carbon and nitrogen. I have thus obtained alkaline-earth nitrides of the general formula NM₃. The barium compound has been obtained pure and crystallised. I am surprised that the power of these metals for the absorption of nitrogen has not been utilised in the preparation of argon.

Crystalline Titanium, and on the Compounds of Titanium and Silicon.—Lucien Lévy.—The author has obtained crystals of the following composition:—Ti, 76.14; Si, 22.69; various matters, 1.27. If we sup-

pose that the various matters are impurities, this would show a composition of Ti_2Si , *i.e.*, 77.42 per cent titanium and 22.58 silicon.

Rotatory Property of Superfused Rhamnose (Isodulcitol).—G. Gernez.—The rotatory power of superfused rhamnose decreases regularly as the temperature rises, and for a variation of temperature of 100° it becomes 61/100 of what it is at 0° .

Certain Dithioazolic Derivatives.—Charles Lauth. The author has formerly obtained methylene blue by causing sulphur to enter into the molecule of the colouring-matter. He has obtained two yellow substances, insoluble in water and ligroine, sparingly soluble in carbon disulphide and benzene, easily soluble in ether, acetone, and alcohol. The alcoholic solution of the base presents a splendid green fluorescence. Both the bases dye a fine yellow both on animal fibre and on unmordanted cotton. The colours resist acids and alkalis, but they are fugitive on exposure to light.

Synthesis of the Hydrochlorates of Amides and of the Chlorides of Acids.—Albert Colson.—The author mixes a nitrile with an acid and saturates the mixture, cooled down to 0° , with dry hydrochloric acid gas.

Action of the Halogens upon Formic Aldehyd.—A. Brochet.—The formation of carbon monoxide appears to be inherent in that of formic aldehyd by the oxidation of methylic alcohol.

Essence of Lemon Grass.—Ph. Barbier and L. Bouveault.—This paper is not suitable for useful abridgment, and is scarcely of sufficient importance for insertion in full.

Respective rôles of Philothion and Laccase in Seeds during Germination.—J. de Rey-Pailhade.—Laccase and philothion, possessing antagonistic chemical properties, meet simultaneously in many seeds capable of rapid growth, and the laccase destroys the philothion by oxidation. The two compounds occur simultaneously in beans, peas, white lupins, wheat, maize, and chestnuts.

Zeitschrift für Anorganische Chemie,
Vol. ix., Part 4.

New Phosphoric Acid, $H_3P_3O_{10}$. Some of its Compounds.—Fritz Schwarz.—Fleitmann and Hinneberg insert between pyrophosphoric and metaphosphoric acids two new compounds, the tetra- and tri-phosphoric acids; whilst decaphosphoric acid is as yet little known. The author describes here a number of tri-phosphates, *i.e.*, those of cobalt, nickel, copper, barium, calcium, and zinc. The attempt to prepare the lead salt of tri-phosphoric acid yielded the tetraphosphate.

Determination of Fluorine by its Expulsion as Hydrofluoric Gas.—P. Jannasch and A. Röttgen.—This paper requires the two accompanying figures.

Separation of Metals in a Current of Hydrochloric Acid.—P. Jannasch and F. Schmidt.

Supposed Group of Inactive Elements.—Julius Thomsen.

Remarkable Change in the Structure of Glass by Heating.—E. Priwoznik.—Among the thin-sided tubes of soda-glass produced for chemical purposes, there are occasionally some which on heating undergo a strange modification of structure. At the temperature of boiling water the upper layer displays both within and without a vast number of fine cracks running in all directions. These cracks do not penetrate deeply into the glass, so that when the scales are rubbed off the body of the tube has not lost much in thickness.

On so-called Amido-chromates.—A. Werner and A. Klein.—The authors express surprise that Dr. S. Löwenthal can have closely examined the amido-chromates, effected transformations with them, and obtained correct analytical results without suspecting that he was simply working with bichromates.

Relations of the Colours of Atoms, Ions, and Molecules.—Carey Lea.—The commencement of this memoir, parts of a paper on the "Nitroso-compounds of Iron," and on some "Iodine Compounds of Lead with excess of Iodine," are wanting. As the main result of Carey Lea's article—which seems to be of profound interest—it is mentioned that: The colour of the elementary atoms is, broadly speaking, a function of the atomic weights. The atoms with atomic weights between:—1—47 are colourless; 52—59, coloured; 65—90, colourless; 103—106, coloured; 112—139, colourless; 145—169, coloured; 192—196, colourless. Elements which fall between these groups have both colourless and coloured atoms.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8. (Cantor Lectures). "Alternate Current Transformers," by Dr. J. A. Fleming, F.R.S.
Medical, 8.30.

TUESDAY, 28th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.

— Society of Arts, 8. "Stamboul—Old and New," by Richard Davey.
— Institute of Civil Engineers, 8.
— Medical and Chirurgical, 8.30.
Photographic, 8.

WEDNESDAY, 29th.—Society of Arts, 8. "Standards of Light," by W. J. Dibdin, F.C.S.
British Astronomical Association, 5.

THURSDAY, 30th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "Dante," by Philip H. Wicksteed, M.A.

FRIDAY, 30th.—Royal Institution, 9. "National Biography," by Sidney Lee.

SATURDAY, Feb. 1st.—Royal Institution, 3. "Realism and Idealism in Musical Art," by Prof. C. Hubert H. Parry, D.C.L., &c.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1888.

PROFESSOR RÖNTGEN'S NEW DISCOVERY.

In the last volume of the *Transactions of the Würzburg Physico-Medical Society*, Professor Röntgen gives an account of his new discovery, which may doubtless prove to be of far-reaching importance in future.

If the discharges of a large Ruhmkorff tube are caused to pass through a Hittorf or a Crookes vacuum tube enclosed in black cardboard case, impervious to sunlight and electric light, as well as to ultra-violet rays, there appears, in a perfectly dark room, at each discharge, an illumination or fluorescence upon a screen coated with barium platino-cyanide. All substances are permeable for this newly-discovered agent, though in very different degrees. Thus the light was perceived behind a book of 1000 pages in thickness, as also behind boards of pine-wood of 2 to 3 c.m. in thickness, even on the introduction of discs of hard caoutchouc of several c.m. in thickness. Among the metals, aluminium was found to be permeable in a high degree, but lead and platinum are permeable only in very thin leaves. A sheet of tin-foil, laid between the apparatus and the screen, is scarcely perceptible. Salts, both solid and in solution, can be arranged in a similar series as regards permeability. Glass plates of equal thickness behave differently according as they contain lead or not; in the former case they are less permeable. Water and carbon disulphide have great permeability. The permeative power of this agent, which Röntgen names the "X rays," depends chiefly on the density of the material. But among metals it was observed that the permeability of different metals is by no means alike when they have the same thickness and density. Besides barium platino-cyanide, fluorescent phenomena are produced by the X rays with uranium glass, common glass, calc-spar, and the calcium compounds included among the phosphorescent bodies. The behaviour of the new rays with photographic plates is especially remarkable. By this use it is practicable to obtain proofs in a *camera lucida* in a closed case, or with plates wrapped up in paper. The photographs of different shadows are interesting; thus we may obtain the image of the bones of the hand by photographing the image of the hand. It is still questionable whether the chemical action upon the salts of silver proceeds directly from the X rays or from the fluorescent light arising in the glass plate, or in the layer of gelatin.

The retina of the eye is not sensitive to the new rays, even if we apply the eye close to the discharging apparatus. Experiments made with water and carbon disulphide in prisms of mica, and again with finely pulverised substances, showed that the X rays are scarcely, or not at all, refracted. Hence the rays cannot be concentrated with a lens. With the reflection of the rays the case is similar. The rays differ from Hittorf's kathode rays, especially by the fact that they are not deflected by the magnet. That part of the wall of the discharging apparatus which fluoresces most strongly must be regarded as the initial point of the X rays. Hence they proceed from the point on which the kathode rays impinge. If the kathode rays are deflected by a magnet within the apparatus, the X rays proceed from another point,—i.e., again from the terminal point of the kathode rays. If the X rays were violet or kathode rays, they must behave quite differently from the ultra-red, the visible, and the ultra-violet rays. Röntgen conjectures that the X rays may be due to longitudinal vibrations of the ether.

Professor Röntgen's X Rays.

In considering Röntgen's discovery, Prof. Boltzmann adheres to the view of the former, and extends his hypothesis, placing along with the three kinds of luminous rays (ultra-red, visible, and ultra-violet) the electric-light waves of Hertz, as transversal, but of greater wave-length. But he claims for the kathode rays and Röntgen's X rays a different nature. In the two latter he recognises longitudinal waves, which in the kathode rays are of extremely short wave-lengths, but of a greater wave-length in those of Röntgen. According to Boltzmann's view, the chief signification of Röntgen's discovery is that we are again made acquainted with a new agency. The discovery of Hertz's rays, and of the kathode rays, has occasioned a justifiable sensation. The former, however, are not essentially different from light waves, and the latter are almost exclusively confined in the narrow limits of the Hittorf tube, and are therefore sparingly accessible either for Science or for practice.

Röntgen's phenomenon is entirely new, and is displayed on a large scale.—*Chemiker Zeitung*.

ANALYSIS OF ALUMINIUM AND ITS ALLOYS.

By HENRI MOISSAN.

THE impurities which we encounter in commercial aluminium profoundly modify its properties, whence it is important to effect its analysis in the most accurate manner possible. The procedures hitherto employed in industry leave for the most part much to be desired, as when we regard as silicon the ferruginous residue which aluminium leaves on treatment with hydrochloric acid, or determine the aluminium as difference.

We have first to examine if the aluminium contains copper. We dissolve a small quantity of aluminium—about 2 grms.—in hydrochloric acid diluted with water, and treat the solution with a current of sulphuretted hydrogen. If the proportion of copper is very small it is useful to heat the solution gently, and to keep it at a hand heat for some hours after the passage of the sulphuretted hydrogen. We filter and search for the copper in the residue.

The qualitative analysis is then conducted so as to show the presence of silicon, iron, carbon, nitrogen, titanium, and sulphur.

1. Aluminium without Copper.

Determination of Silicon.—We weigh out about 3 grms. of the metal, which is then treated with pure hydrochloric acid diluted to one-tenth. If there remains a residue of a grey colour (containing silicon, iron, aluminium, and carbon) we separate this powder and attack it with a small quantity of melting sodium carbonate in a platinum crucible. The contents of the crucible are taken up in dilute hydrochloric acid, and this solution is added to the former. The liquid is put in a porcelain capsule and kept on the water bath until dry. The capsule is then placed in a hot air stove at the temperature of 125°. The residue should then be absolutely white, pulverulent, and should not adhere to the stirring rod. To obtain this result it is advisable to scrape the sides of the capsule with a spatula of platinum, and to crush any clots with an agate pestle. We remove the capsule after it has remained for 12 hours in the hot air stove, when it is observed that a stirring-rod moistened with ammonia and held above the residue no longer gives off dense white fumes, indicating that all escape of hydrochloric acid has ceased.

The desiccation being completed we take up the residue in luke-warm distilled water, to which has been added the smallest possible quantity of hydrochloric acid. The liquid is heated to ebullition for a few minutes, the silica remains insoluble and is thrown on a filter. After washing it is ignited and weighed. To be certain that this

silica does not contain alumina or ferric oxide we pour pure hydrochloric acid into the platinum crucible used in the last ignition. After evaporation to dryness in the sand bath no residue should be left.

Determination of Aluminium and Iron.—The original solution of the aluminium in dilute hydrochloric acid, after the separation of the silica, was diluted with water to the volume of 500 c.c. Of this solution we take 25 c.c., corresponding to 0.150 grm. of aluminium, neutralise it with ammonia in the cold, and precipitate the two oxides with recently prepared ammonium sulphide. The mixture is left to digest for an hour. The precipitate is then thrown upon a filter, washed, dried, ignited, and weighed.

We do not employ ammonia for this precipitation, for if it is to be complete the solution must not be too dilute, and must contain a sufficiency of ammonium salts and very little free ammonia. We may, indeed, get rid of the excess of ammonia by ebullition, but in this case we must stop when the liquid is only slightly alkaline, for if we exceed this point the alumina reacts slowly upon the ammoniacal salt, and the liquid takes an acid reaction. On account of these difficulties we prefer the precipitation with ammonium sulphide.

The precipitated alumina is very difficult to wash. It is necessary to effect the washing by decantation with boiling water in a cylindrical beaker of Bohemian glass. The washing is complete when the supernatant liquor no longer contains chlorine. The precipitate is then placed on a filter, dried, calcined, and weighed. We thus obtain the joint weight of the alumina and the ferric oxide contained in the aluminium. The iron is at first precipitated as a hydrated sulphide, but it is quickly oxidised by the washing and ignition.

It is very important to dry this alumina carefully before heating it to redness. The ignition must be effected slowly, because alumina if heated strongly sometimes decrepitates. Lastly, the ignition must be carried far enough, because alumina loses its water only under the action of a very high temperature.

Determination of the Iron.—To determine the iron we take 250 c.c. of the original solution after the separation of the silica. This liquid is reduced by evaporation to about 100 c.c. We add caustic potassa quite free from silica, which precipitates at first the iron and the alumina, and when in sufficient excess re-dissolves the latter.

The mixture is kept for ten minutes at a temperature close upon ebullition. The precipitate is washed by decantation five or six times with boiling water, and is then thrown upon a filter. It is re-dissolved in dilute hydrochloric acid and again precipitated with an excess of potassa. After washing and filtration it is again dissolved in hydrochloric acid, and this time the iron is precipitated with ammonia.

The precipitate is brought upon a filter, washed, ignited, and weighed. Proportionally we deduct from the weight of the two oxides obtained in the foregoing operations the weight of the ferric oxide, and the difference shows the weight of the alumina.

Determination of Sodium.—The method of determination is founded on the fact that the aluminium nitrate is destroyed by heat, yielding alumina at a temperature below that at which sodium nitrate is decomposed.

We take 5 grms. of aluminium—whether containing copper or not—in filings or in sheets; we treat them in a conical vessel with nitric acid diluted with an equal volume of water, applying a gentle heat. The action does not take place in the cold, but the temperature must be raised cautiously, as otherwise the disengagement of gas may be violent.

The solution is concentrated in a platinum capsule on the water bath, and then evaporated to dryness on the sand bath or over an open fire. The residue is brought to a pulverulent state by means of an agate pestle.

We heat then at a temperature which is below the fusion point of sodium nitrate until all escape of nitrous vapours has ceased. We then dissolve in boiling water,

decant the liquid, and wash the alumina three or four times.

At the same time we wash the pestle and the capsule, and all the washings, with the addition of a few drops of nitric acid, are evaporated to dryness. We dissolve three times in boiling water, each time eliminating a fresh quantity of alumina which has been mixed with the alkaline nitrate. Lastly, we treat with boiling water, evaporate in a porcelain capsule, add a slight excess of pure hydrochloric acid, and evaporate to dryness. We add a further quantity of hydrochloric acid, and after evaporation heat to 300° to expel any excess of acid. The sodium chloride remaining is determined as silver chloride. From the weight of the latter we deduct its quantity of chlorine, and calculate its equivalent weight of sodium.

Determination of Carbon.—We take 2 grms. of the metal in state of shavings or filings, triturate them in a mortar with from 10 to 15 grms. of mercuric chloride in powder, with the addition of a small quantity of water. The mixture is evaporated in a capsule on the water bath, and afterwards placed in a porcelain boat, which is then heated in a current of pure hydrogen. This boat is put into a tube of Bohemian glass and heated to redness. The gaseous current traverses a Liebig tube containing a solution of potassa and two small U-tubes filled with fragments of potassa. The increase of weight in these tubes gives in carbonic acid the quantity of carbon contained in the aluminium.

2. Analysis of Alloys of Copper and Aluminium.

When the alloy contains up to 6 per cent of copper we dissolve 0.5 grm. of the metal in nitric acid perfectly free from chlorine, we dilute the solution to the volume of 50 c.c. and effect the determination electrolytically. The current employed has an intensity of 0.1 ampère; the operation takes 6 hours at the temperature of 60°, or 24 hours in the cold. When the electrolysis is completed the copper is washed, dried, and weighed as metal.

Determination of Silicon, Aluminium, and Iron.—The author subjoins the analysis of a sample of aluminium from Pittsburgh:—

Aluminium	98.82
Iron	0.27
Silicon	0.15
Copper	0.35
Sodium	0.10
Carbon	0.41
Nitrogen	traces
Titanium	traces
Sulphur	—
	100.00

A sample made at Neuhausen two years ago contained:—

Aluminium	96.12
Iron	1.08
Silicon	1.94
Carbon	0.30
	99.44

Along with the analytical results we must take into account mechanical data, extensibility, limit of elasticity, and breaking weight.—*Comptes Rendus*, cxxi., p. 851.

The "Pli Cachete" System.—The *Chemiker Zeitung* announces that it has opened a department for taking charge of sealed documents, containing a sketch of some incomplete scientific investigation which is not to be opened and made known except at the request of the author. This system has long been in use by scientific societies and journals in France. The object proposed is to furnish evidence in the case of dispute as to the priority of any discovery or invention. The system is, however, open to an abuse which we have pointed out on a former occasion.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 40.)

The Electric Spectrum of Lithium.—I wished to check my results by replacing the heat made by the burning oxy-hydrogen gas, by a spark from a small induction coil *without a condenser*, as M. Lecoq de Boisbaudran and M. Bunsen had already done when using chloride instead of oxide. For this purpose, after having carefully eliminated the sodium from the oxide of lithium, with an oxy-hydrogen blowpipe, and *whilst it was still heated up to the fusing-point of platinum*, I put into the liquid two balls of pure platinum, 3 m.m. diameter, attached to thick platinum wires, which had just been made white-hot and quickly cooled, so as to cover the balls with a fairly thick layer of oxide of lithium.

Having fixed the two balls at a convenient distance apart (from 2 to 3 m.m.), and in front of the Steinheil and Duboscq spectroscopes, I passed an induction spark between the two balls, by means of a small coil *without condenser*, and as strong as could be used without showing air lines: although the spark was *hardly coloured purple*, I recognised simply and solely the lines of the incandescent hydrogen flame spectrum, neither more nor less,—that is to say, *the sodium line was entirely absent*, but the three red, orange, and pale blue lines appeared. Notwithstanding that the number of lines in the electric and complete flame spectra of oxide of lithium is the same, there is yet a fundamental difference between the two spectra. In the flame spectrum the red line is very strong and brilliant, and the orange or yellow line is very weak, whilst in the electric spectrum it is the other way about—the red line is very weak, and the orange line is strong and brilliant. I saw no difference between the strength and colour intensity of the blue line in either spectrum. It is thus certain, as follows also from Bunsen's observations, that there is an essential difference between the *appearances of the two lithium spectra*. As for the *position of the lines in the flame and electric spectra*, I found them identical when taking the *solar spectrum as a standard of comparison for the two lithium spectra*.

Wishing to ascertain whether the spectrum of lithium would be changed by substituting a strong discharge for the spark from the small coil without a condenser, I replaced the small coil by a large Ruhmkorff coil with a condenser composed of five very large Leyden jars, taking care to adjust the solar spectrum previously as a standard of comparison.

Whether I allowed or stopped the passage of solar rays, I found the lithium spectrum identical, as regards the *number and position of the lines*, with that in the oxy-hydrogen blowpipe, with the addition, however, of some air lines; but at the same time I noticed an undoubted appearance, though extremely faint, of the sodium lines corresponding to the D and D₂ lines in the solar spectrum. When trying to account for the appearance of the sodium lines, I found that, on substituting pure platinum balls for those coated with oxide of lithium, spectrum analysis of a discharge showed the sodium lines in the *same atmosphere*, with the same degree of clearness as when passing through oxide of lithium. *I repeated this comparison several times, and always with the same result.* During this time, spectrum analysis of a Bunsen flame, burning in this same atmosphere, did not show a trace of the sodium line. Unfortunately, the contamination of the air by the presence and movement of the *three people* necessary for making observations, soon put an end to the experiments.

These investigations date from the month of December, 1878. I repeated them at different times, when the air was sufficiently pure, using in succession a spectroscope with one prism, and one with five prisms by M. Duboscq,

and I must say that I never worked in Brussels in indoor air, or even outer air, which was sufficiently free from sodium as not to give, during spectrum analysis of a *strong discharge*, unmistakable though faint signs of the presence of sodium, although it was absolutely impossible for me to see the sodium line in the same air with a Bunsen burner, or a spark from a small coil which did not show any air lines.

In this way are explained the facts mentioned above about platinum, silver, &c., which, when completely freed from sodium and then kept in air, attract this metal from it, and give, after a certain time, on spectrum analysis, absolute proofs of the presence of sodium. I call the appearance of the double D line an absolute proof. Thus also are confirmed the facts mentioned in the chapter "On the Nature and Amount of Soluble and Insoluble Mineral Matters in the Air of the Upper Part of Brussels," &c.

The possibility of ascertaining whether sodium be or be not present in the air, depends therefore on the amount of the metal in it, and on the method used to discover it.

I can see no other explanation of these phenomena. For instance, oxide of lithium, when freed from sodium by the method I have described, and left in air *sheltered from floating dust*, unmistakably shows the sodium line, after a time which varies according to the relative purity of the air; platinum balls coated with oxide of lithium act in the same manner. After being kept for several days under a bell-jar, they showed the sodium line in a spark from a small coil, just as though the oxide used had never been freed from sodium.

When checking my observations, in collaboration with M. Depaire, I had an opportunity for observing the same facts when using pure sulphate of lithium made by M. Bunsen. We then found that this sulphate, when heated on platinum balls, showed the sodium line faintly or not at all *in the same air*, according as it was used in a spark with or without a condenser, and that the coated balls, when left in air protected from dust, showed, with a spark *without a condenser*, on the next day, the sodium lines due to the sodium they absorbed from the air.

I have mentioned above that the spectrum of lithium in an electric discharge is identical with that in a weak spark. Since this paper was written Messrs. Liveing and Dewar have found a second blue line in the spectrum of lithium in an electric arc; we had therefore to re-examine the spectrum of lithium in the discharge, to ascertain whether there was, or was not, a difference between the lithium spectrum in a spark or discharge, and that in an electric arc.

It follows from the above facts that, under conditions where accurate experiments are possible without absorbing sodium from the surrounding medium, there is no connection between the characteristics given to flames by lithium in the form of oxide or sulphate, and that given by sodium compounds. Lithium and sodium are not convertible the one into the other; they behave like distinct bodies.

As for the spectrum of lithium, it is clear that the flame spectrum varies with the temperature in which the metallic compound is vaporised.

When using an analyser, of which the eyepiece, prisms, and lenses are of flint-glass, the spectrum of a weak or strong spark is identical with the complete flame spectrum (1879). The recent discovery by Messrs. Liveing and Dewar, of a second blue line in the lithium spectrum of an electric arc, renders new researches on the lithium spectrum in an electric discharge absolutely necessary.

When trying, with M. Depaire, whether it was possible, in the lithium spectrum in an electric discharge, to see the second blue line discovered by Messrs. Liveing and Dewar, using for the purpose, successively, a single prism spectro-scope,—the same as that used by M. Lecoq de Boisbaudran in his researches,—then one of Messrs. Liveing and Dewar's direct vision spectroscopes, made by M. Hilger, our investigations were fruitless, whether we worked in

air and allowed for atmospheric lines, or caused the discharge after replacing the air by hydrogen.

In both cases we found, *beyond a doubt*, only a single blue line—that discovered by Messrs. Frankland and Lockyer. The result was quite different when substituting one of M. Hilger's spectroscopes with two half-prisms and eyepieces of quartz, for Duboscq's and the direct-vision spectroscope, both fitted with very refractive and absorbent flint-glass prisms. When using this fine instrument, we saw the second blue line, not only in the electric discharge, but even in a spark *without* a condenser, charged with lithium. The second line appeared, in this case, of a very pale blue tint.

The visibility or non-visibility of this second blue line in the spark or discharge spectrum, depends then entirely on the *analyser*. We have already mentioned that, when using M. Hilger's spectroscope with quartz prisms and lenses, we did not see the second blue lithium line in a flame spectrum (inner cone of lithium charged oxy-coal-gas). These facts being determined, it was hardly necessary to submit a lithium charged electric arc to spectrum analysis. Nevertheless, we undertook this research, for the purpose of satisfying ourselves as quickly as possible as to the influence of luminosity and of the analyser, and the permanence of the lithium spectrum.

With this object we made:—

1st. An electric arc by means of 33 Julien accumulator cells, giving at the terminals 10 ampères and 70 volts.

2nd. An electric arc by means of a gramme and Siemens's dynamo *coupled*, giving at the terminals 28 ampères and 70 volts.

In both cases, the electric arc passed between two pure carbon electrodes, consuming them without leaving a trace of ash; they were used in a Foucault lamp. The negative electrode, from 6 to 7 m.m. diameter, ended in a point; the positive electrode, about 12 m.m. diameter, ended in a flat surface, in which a small hole was drilled to receive the lithium compound to be volatilised in the arc.

As analysers, one of us used M. Hilger's spectroscope with two half-prisms and lenses of quartz, and the other Messrs. Liveing and Dewar's direct-vision spectroscope with flint-glass prisms.

After making the arc by putting the electrodes in contact, thus causing the fusion of the sulphate and chloride of lithium in the hole in the positive electrode, we saw, first with the current from the accumulator, then with the current from the *coupled* dynamos, the lithium spectrum, composed of its *four* lines (one dark red line, one orange-yellow line, the first pale blue line, and a second blue line paler than the first), appear, either on a very bright *continuous* spectrum, or on a *continuous* spectrum partially masked by the carbon spectrum of fine brilliant lines. These fine lines were as M. Fievez described them in his "*Recherches sur le Spectre de Carbone dans l'Arc Electrique*," and as Lieutenant-General Liagre and one of us had seen them whilst M. Fievez was carrying on his work at the Royal Observatory at Brussels.

In order that we might be able to carry on our observations for the time necessary to identify the lithium and carbon lines, an assistant was told off to introduce the lithium compound into the arc as it became volatilised, by means of a pure carbon rod. When the lithium compound was being introduced into the interior of the electric arc, it did not change colour, whilst the envelope was coloured deep red, especially towards the negative electrode. At the temperature of the electric arc, therefore, lithium vapour is blue, like the arc itself.

When working in this manner, we were able to demonstrate to certainty that the background of the spectrum consisted of a lithium spectrum on a continuous spectrum, or of a lithium spectrum on a continuous spectrum, masked by the fine lines caused by the resolution of the carbon bands, according as the electrodes *touched* or were *separated*,—that is to say, according as spectrum analysis

was made of the electrodes in contact but surrounded by lithium vapour, or of the arc containing vapours of carbon and lithium simultaneously. But in both positions of the electrodes, we saw the four lithium lines permanently, no more, no less.

One must therefore conclude that the spectrum of lithium, in an arc as powerful as we had at command, is permanent.

When using sulphate of lithium absolutely free from sodium, we did not see the double sodium lines in the spectrum; whilst when using chloride of lithium containing sodium, we found the double sodium lines in the spectrum.

(To be continued.)

ON THE OXIDATION OF SOME GASES WITH PALLADINISED COPPER OXIDE.*

By E. D. CAMPBELL.

(Continued from p. 33).

IN determining the rate of combustion of any gas the method was as follows:—The tube filled with air was carefully brought up to the temperature at which combustion was to be made, and maintained at this temperature until thoroughly heated through. A weighed calcium-chloride tube was attached to the outlet of the combustion-tube, followed by a double Liebig potash-bulb. The latter was made by uniting two ordinary Liebig bulbs and placing in the first bulb a solution of potassium hydroxide (1 : 2), and in the second bulb a stronger (1 : 1), the bulb being provided with the usual guard-tube. It was found necessary to have the potassium hydroxide in the first bulb more dilute than 1 : 1, since most of the carbon dioxide was taken up in the first small bulb, and if 1 : 1 potassium hydroxide was used potassium acid carbonate crystallises out so as to choke the tube. By using the more dilute solution in the first bulb the trouble is avoided. When the combustion-tube has attained the desired temperature, the pure gas under examination was forced through the tube, the rate at which it is supplied being so regulated that as light excess of unburned gas passes completely through the train. In the combustions shown in the table this excess of unburned gas was judged by the number of bubbles passing through the last small bulb of the potash bulbs, and the supply of gas was so regulated that this excess should come through at the rate of 6 to 10 bubbles per minute. The exact time at which the gas was introduced into the combustion-tube was noted. The gas at the commencement was introduced rather rapidly for a few moments to expel the air in the tube, then the flow regulated to the 6—10 in excess and kept up for times varying from 45 minutes to 6 hours, according to the rate at which the gas burned. At the end of an exact time, the stopcock was reversed and pure air drawn through the tube until all the products of combustion had been collected. From the weight of water and of carbon dioxide or of both obtained, the number of c.c. of pure gas required to produce these was calculated. In addition to the number of c.c. of each gas burned per hour has been calculated the weight of oxygen removed from the copper oxide for the combustion. In order to determine the extent to which palladium effected combustion, the ignition-point of the various gases was determined by passing the gas over a long plug of pure copper oxide made by oxidising pure copper gauze. This copper oxide was contained in a combustion-tube of the same size and heated in the same way as the one containing the palladinised copper oxide. It will be noted that the ignition-point of hydrogen has been reduced about 95°, that of

* Contributions from the Laboratory of Analytical Chemistry of the University of Michigan. From the *American Chemical Journal*, vol. xvii., No. 9, November, 1895.

ethylene 75°, of propylene 50°, of isobutylene 40°, while that of carbon monoxide, as would be expected, has not been affected.

In the preparation of gases the following methods were used:—

I. Hydrogen was prepared by the action of dilute sulphuric acid on pure zinc, and purified by passing through potassium hydroxide (1 : 1), over dry potassium hydroxide, calcium chloride, and phosphorus pentoxide.

II. Carbon monoxide was prepared by the action of strong sulphuric acid upon oxalic acid, the carbon dioxide being removed with potassium hydroxide, and the gas being then purified in the same way as the hydrogen.

III. Ethylene was prepared by the action of ethyl alcohol upon phosphorus pentoxide, and purified by passing through strong potassium hydroxide and then over three towers of dry potassium hydroxide. It was found in the course of the work that if phosphorus pentoxide was used in the train that there was some polymerisation with ethylene, and that this tendency to polymerise increases with propylene, and was so marked with isobutylene as entirely to prevent the use of phosphorus pentoxide. Ethylene produced from alcohol and sulphuric acid in the usual manner was found to contain so much carbon monoxide as to be unfit for this work, while that produced by the method used was shown by analysis to be practically pure.

IV. Propylene was prepared by carefully heating propyl alcohol and phosphorus pentoxide and purifying as in the case of ethylene. This method gives very nearly if not quite pure propylene.

V. Isobutylene was prepared by the action of isobutyl iodide upon alcoholic potash, the gas being collected over a 10 per cent solution of common salt, and then purified in the same way as ethylene and propylene. When an attempt was made to obtain isobutylene by the action of the corresponding alcohol upon phosphorus pentoxide, it was found the resulting gas contained only about 60 per cent of isobutylene and 35 per cent of butane.

VI. Methane was prepared by the action of methyl iodide on zinc-copper couple immersed in alcohol. It was purified by passing through strong sulphuric acid containing chromic acid and then through strong potassium hydroxide, followed by dry potassium hydroxide and phosphorus pentoxide.

VII. Acetylene was prepared by the action of calcium carbide on water. It was purified and dried by passing through strong potassium hydroxide and then over dry potassium hydroxide.

The details of the temperature and rate of combustion of the above gases, except ethylene, which does not oxidise perfectly to carbon dioxide and water, are shown in the following table. All rates of combustion have been calculated from the weight of water or carbon dioxide obtained to the c.c. of pure dry gas, under standard conditions, which would be burned in one hour. Since these combustions were all made in the same sized tube, and with practically the same amount of surface of copper oxide exposed, the rates of combustion are comparable. Of course varying the size of the combustion-tube, and with it the amount of palladinised copper oxide present, would alter the absolute rates of combustion, but would probably not effect the relative rates.

(To be continued).

A SIMPLIFIED METHOD OF DETERMINING PHOSPHORIC ACID BY MEANS OF MOLYBDENUM SOLUTION.

By J. HANMANN.

THE author determines phosphoric acid by weighing directly the precipitate of ammonium phosphomolybdate. The method presupposes that no molybdic acid is sepa-

rated along with the ammonium phosphomolybdate. To prevent such a precipitation of molybdic acid we may precipitate a portion of the molybdic acid by previously repeated boiling from a molybdenum solution prepared according to Sonnenschein's formula, and then precipitate the phosphoric acid in heat with the molybdic solution over-charged with nitric acid. Or we may use a molybdic solution in the cold, which, after long and vigorous agitation of the mixed liquids, deposits all the phosphoric acid of the solution as a precipitate of constant composition.

As a matter of fact, it is possible to precipitate in the cold all the phosphoric acid, by vigorous agitation for half-an-hour with a solution of molybdenum containing to 100 grms. molybdic acid 1 litre of 10 per cent ammonia and 1½ litre nitric acid of sp. gr. 1.246, or with Maercker's solution, to which more ammonia has been added. The precipitate thus obtained, which is washed with a solution of ammonium nitrate, acidified with nitric acid, and dried, takes, on gentle ignition, a pure black-blue colour, and is constant in its composition, containing, in 100 parts by weight, 4.018 parts by weight of phosphoric acid. It is recommended to use the smooth compact filters of the firms Dreverhoff or Schleicher and Schull, as they allow of the precipitate being very completely removed from the paper, which is then burnt separately.

If the precipitate, after a gentle ignition, has not the proper blackish blue colour, it is moistened with a little ammonia, dried, and ignited again.

Organic matter is destroyed, before precipitation, by boiling with nitric or chromic acid. The ignition of the precipitate may be effected in a platinum crucible, or preferably on a net of platinum wire. The bottom of the crucible must not appear red-hot, though the wire net should. The method permits of the employment of very small quantities. The author has used it very successfully for superphosphates and arable soils.—*Chemiker Zeitung*.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 19th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 46).

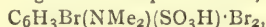
152. "Researches on Tertiary Benzenoid Amines. I. Derivatives of Dimethylaniline." By CLARA DE BRERETON EVANS, B.Sc.

It is now established in the case of primary and secondary benzenoid amines, that the production of derivatives containing a substituent in the hydrocarbon nucleus is often preceded by that of the corresponding derivative in which the substituent is present in the amino-group; and inasmuch as compounds of the latter readily pass over into those of the former class, it is not improbable that their formation is a necessary step in that of many derivatives of benzenoid amines. As it is impossible, however, that similar derivatives should be formed from tertiary amines, the behaviour of these is of interest as throwing light on the influence which nitrogen itself exercises; and that this may be altogether different from that of nitrogen associated with hydrogen is clear from a comparison of benzenoid amines with *asophenes* (compare *Proc. Chem. Soc.*, 1892, 128) such as pyridine and quinoline, as these latter manifest a comparative indifference towards agents generally which is quite remarkable.

The experiments to be described have brought to light the fact that tertiary benzenoid amines manifest a somewhat similar indifference.

Dimethylaniline is readily sulphonated by means of chlorosulphonic acid, yielding only the *para*-acid; it is somewhat less readily, but yet easily sulphonated by means of a single molecular proportion of ordinary sulphuric acid, but if a larger proportion of acid be used, the action takes place less readily, sulphonation being incomplete at the end of *twelve hours* at 180° when five molecular proportions of acid are used, although it is complete within *five hours* when a single proportion is taken. Practically nothing but the *para*-acid is formed. To procure the *meta*-acid, it would seem that it is necessary to use fuming sulphuric acid—a point of some interest in connection with the moot question as to the manner in which isomeric sulphonic acids are generated. The behaviour of diethylaniline is similar to that of dimethylaniline.

The behaviour of the *para*-acid towards bromine is remarkable. It first yields a *monobromo*-acid. On adding bromine to a solution of this bromo-acid in muriatic acid, a crystalline orange-coloured perbromide,—



is precipitated. This is readily and simply deprived of its bromine by exposure to air, by boiling with water, and in contact with ammonia, sulphurous acid, or potassium iodide. If digested with muriatic acid on the water-bath in a closed vessel, it yields a small amount of tribromomethylaniline and some tetrabromodimethylaniline, together with much unchanged monobromo-acid; if digested with excess of bromine, it is entirely converted—but by no means easily—into tetrabromodimethylaniline. Under no condition, apparently, does it yield a dibromosulphonic acid or tribromodimethylaniline; in this respect its behaviour is most remarkable in comparison with that of ordinary sulphanilic acid, which is extremely sensitive to the action of bromine, being very readily converted into tribromaniline.

The *meta*-acid, in like manner, readily yields a *para*-bromo-acid identical with that obtained on sulphonating parabromodimethylaniline, and this is converted into a dibromo-acid by the further action of bromine. But all attempts to prepare a tribromo-acid corresponding to that which is so readily obtained from anilinemetasulphonic acid were unsuccessful. No perbromide is obtained from the metabromo-acids.

On nitration with nitric acid, dimethylanilineparasulphonic acid yields a mixture of orthoparadinitrodimethylaniline, together with orthonitroparasulphonic acid, the latter being the chief product. The *meta*-sulphonic acid yields a dinitrosulphonic acid. On warming a solution in dilute acetic acid of the orthonitroparasulphonic acid with bromine, a substance crystallising in red prisms, melting at 102°, is produced, which apparently is a bromonitromethylaniline.

The behaviour of the diethylanilinesulphonic acids is similar to those of dimethylaniline. The perbromide derived from the bromoparasulphonic acid is better characterised even than that derived from the dimethylated acid.

A full description of the various compounds referred to in this note will be given in a complete paper; it may be stated that all are exceedingly well-defined substances.

Experiments are in progress having for their object the comparison of the ortho-acids of dimethyl- and diethylaniline with the isomeric *meta*- and parasulphonic acids; and others are being made with the secondary amines to ascertain if their behaviour be, as is probable, similar to that of primary amines rather than intermediate between that of primary and tertiary. It is also proposed to largely extend these observations to other tertiary aminobenzenoid compounds, such as the dimethyltoluidines, dimethylamidophenol, and dimethylamidobenzoic acid.

For the supply of a large quantity of material used in these experiments, Dr. Armstrong is indebted to the Société pour l'Industrie Chimique à Bâle.

153. "Experiments on the Formation of the so-called Ammonium Amalgam." By JAMES PROUDE and W. H. WOOD, F.I.C.

The fact, first clearly established by Wetherill, that sodium amalgam does not form the so-called ammonium amalgam when added to an aqueous solution of ammonia, enables sodium amalgam to be used as a test for the presence of ammonium salts, even in the presence of ammonia.

Solutions of phenol and of pyrogallol in aqueous ammonia were shown to contain compounds of the nature of ammonium salts; whilst sodium phosphate, calcium chloride, and magnesium sulphate, with aqueous ammonia, gave rise to no mercurial froth, showing absence of ammonium salts.

Ammonium sulphate, nitrate, and acetate when fused gave no mercurial froth on the addition of sodium amalgam. Ammonium chloride, oxalate, acetate, benzoate, tartrate, and succinate, dissolved in absolute alcohol, rectified spirit, and methylated spirit, in no case gave a definite mercurial froth with the sodium amalgam, either cold or hot, though the acetate and benzoate dissolved in rectified spirit, and the chloride in methylated spirit, showed indications of swelling of the mercury. Water, therefore, appears to be necessary to the production of a definite froth.

The sp. gr. of the well-formed mercurial froth is not higher than 0.730, since it floats in methylated ether of that density.

154. "The Molecular Volumes of Organic Substances in Solution." By W. W. J. NICOL, M.A., D.Sc.

In 1883, and again in 1892, the author directed attention to the probability that a study of the molecular volumes of organic substances in solution would lead to results from which the atomic volumes of the various elements could be determined with an ease and accuracy impossible by Kopp's method of determining the volume at the boiling-point.

The paper contains an account of determinations made on fourteen esters in dilute solution in various solvents. The chief conclusions drawn are as follows:—

1. The volumes of isomeric esters are approximately the same.
2. The volume of CH_2 is a constant for each solvent, being 16.8 in xylene, 17.0 in benzene, 17.3 in 88 per cent alcohol, except
3. In the case of ethyl oxalate and succinate, where the value is about a unit less, owing probably to contraction resulting from the separation of the two carboxyl groups.
4. The nature of the solvent has a marked effect on the molecular volume, which is less in the solvent with the higher molecular weight.

155. "2 : 1 β -Naphthylaminesulphonic Acid and the corresponding Chloronaphthalenesulphonic Acid." By HENRY E. ARMSTRONG and W. P. WYNNE.

Tobias has recently shown (Germ. Pat. 74,688, February 19, 1893) that the acid obtained by one of us (Armstrong, *Ber.*, xv., 1882, 202) by the action of chlorosulphonic acid on β -naphthol at the ordinary temperature is not β -naphthylsulphuric acid, $\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{SO}_3\text{H}$, but the isomeric 2 : 1- β -naphtholsulphonic acid, and in the same patent has described the amido-acid obtained by heating the hydroxy acid with strong aqueous ammonia under pressure at 220–230°. Being desirous of examining the amido-acid, the authors applied to Dr. Tobias for a sample, and he not only sent them a carefully purified specimen of the sodium salt of the β -naphthylaminesulphonic acid, but courteously forwarded their letter to the Farbwerke vorm. Meister, Lucius, and Brüning, who, with characteristic liberality, furnished them with a considerable quantity of the technical product. After purification, the acid was found to have all the characters described in the patent; its sodium salt, as there stated, crystallises from dilute alcohol in monohydrated scales.

The acid was converted by the Sandmeyer method into the corresponding 2 : 1- β -chloronaphthalenesulphonic acid, which has not hitherto been described, and is the twelfth of the fourteen isomerides which it is theoretically

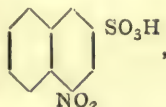
possible to isolate. This acid yields an easily soluble mono-hydrated microcrystalline barium salt, a mono-hydrated potassium salt crystallising in thin scales, and a monohydrated sodium salt crystallising in long slender needles. The chloride, $\text{Cl} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_2\text{Cl}$, crystallises from a mixture of benzene and light petroleum in large tabular forms, and from acetic acid in diamond-shaped scales melting at 76° ; it yields an amide crystallising in slender needles melting at 153° , and on distillation with phosphorus pentachloride is converted into 1:2-dichloronaphthalene, melting at 35° .

On sulphonation with four times its weight of cold 20 per cent anhydrosulphuric acid, the 2:1- β -naphthylaminesulphonic acid is converted into the 2:1:4'- β -naphthylaminedisulphonic acid, previously described by the authors as the minor product of sulphonation of the Dahl 2:4'- β -naphthylaminesulphonic acid under similar conditions (*Proc. Chem. Soc.*, 1890, 129).

The investigation of the 2:1- β -naphthylaminesulphonic acid and its derivatives is being continued.

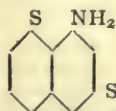
156. "1:3- α -Naphthylaminesulphonic Acid and the corresponding Chloronaphthalenesulphonic Acid." By HENRY E. ARMSTRONG and W. P. WYNNE.

In the course of their study of the formation of isomeric naphthylene derivatives, the authors had occasion to attempt the repetition of Clève's work on the nitration of naphthalene- β -sulphonic acid, since of the three acids obtained by him in this way, one was stated to have the constitution—



the other two being the isomeric heteronuclear α -nitroacids. Whilst successful in obtaining two heteronuclear acids, of which they determined the constitution, they were unable to prepare the homonuclear compound by the nitration of potassium naphthalene- β -sulphonate (*Proc. Chem. Soc.*, 1889, 17). Particular interest attached to the question whether this acid was formed, inasmuch as—to repeat the words used at the time—"it has always been found that a heteronuclear α -derivative is formed in cases in which the corresponding benzene derivative would afford a meta-derivative." Although thus unsuccessful, they were, as they then said, "loth to accept the apparently logical interpretation of their results, as they were unacquainted with the precise conditions under which Clève worked . . . and as it is within their own experience that slight variations in treatment, such as may escape notice, may materially affect the result," and expressed the hope that Clève would supply further details as to the procedure adopted by him. Subsequently it came to their knowledge that the homonuclear acid also could not be detected in the product obtained on nitrating sodium naphthalene- β -sulphonate on the large scale. Moreover, Erdmann and Süvern have failed to obtain the corresponding chloride by nitrating naphthalene- β -sulphonic chloride (*Annalen*, cclxxv., 252).

It is particularly instructive, therefore, to record the fact that the so-called $[\gamma]$ naphthylaminesulphonic acid which Clève prepared by reducing the homonuclear nitroacid he obtained by nitrating sodium naphthalene- β -sulphonate (*Ber.*, xix., 2179; xxi., 3271) is identical with the 1:3- α -naphthylaminesulphonic acid of Kalle and Co.'s German Patent 64979, prepared from α -naphthylamine- $[\epsilon]$ -disulphonic acid—which the authors have shown has the constitution—



(*Proc. Chem. Soc.*, 1890, 15)—by partially hydrolysing it with diluted sulphuric acid, and which, as Friedländer

has recently shown, may also be obtained by partially reducing the said disulphonic acid with sodium amalgam (*Ber.*, xxviii., 1951).

Through the kind offices of Dr. Hepp, the authors are much indebted to Messrs. Kalle and Co. for a supply of this acid in the pure form; the experiments they have made with it confirm Clève's statements as to the properties of this acid and the derived 1:3- α -chloronaphthalenesulphonic acid in every particular. There is nothing to add to the description of the salts of the amido- and chloro-acids as given in Clève's later paper, but the authors have been able to carry the identification of the acids a stage further, since they find that the dichloronaphthalene, melting at 61.5° —obtained from the chloronaphthalenesulphonic chloride melting at 106° —on sulphonation gives products characteristic of 1:3-dichloronaphthalene (*Proc. Chem. Soc.*, 1890, 82) and not of the 1:2'-isomeride of about the same melting-point with which it was for a while confused.

157. "Studies on the Constitution of Tri-derivatives of Naphthalene, No. 15. The Disulphonic Acids obtained by Sulphonating 1:3- α -Naphthylamine- and 1:3- α -Chloronaphthalene-sulphonic Acids." By HENRY E. ARMSTRONG and W. P. WYNNE.

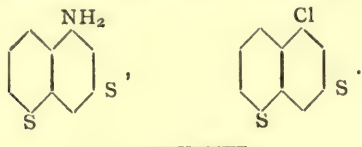
As already announced (*Proc. Chem. Soc.*, 1890, 18, 131, 133; *Brit. Assoc. Report*, 1893, 382, footnote), the authors are engaged on experiments having for their object the determination of the comparative influence exercised by the radicles Cl, OH, and NH_2 , in naphthalene derivatives on the formation of disulphonic acids. Certain results arrived at in the case of β -derivatives have already been communicated (*Proc. Chem. Soc.*, 1890, 128, *et seq.*), but progress with the work was retarded so long as the characteristics of the reference compounds—the trichloronaphthalenes—were in doubt. The fourteen theoretically possible isomerides being now known and characterised (*Proc. Chem. Soc.*, 1895, 84), the authors hope shortly to complete their investigation of the products obtained on sulphonating the known naphthylamine- and chloronaphthalene-sulphonic acids. In the meanwhile, in view of the interest attaching to the 1:3- α -naphthylamine-sulphonic acid, they think it well to put on record the results obtained on sulphonating it and the corresponding chloro-acid, so far as their experiments have gone.

When dry 1:3- α -naphthylaminesulphonic acid is stirred into four times its weight of 20 per cent anhydrosulphuric acid at a temperature not exceeding 20° , it is converted in the course of 12 hours into what appears to be a single disulphonic acid. The normal potassium salt being very soluble, the acid was isolated in the form of the dihydrated acid potassium salt, which crystallised in radiate groups of short brittle needles. On reduction by the hydrazine method it gave naphthalene-1:2'-disulphonic acid (*Proc. Chem. Soc.*, 1890, 126) since the chloride obtained from it crystallised from acetic acid in glistening scales, melting at 122° , convertible by phosphorus pentachloride into 1:2'-dichloronaphthalene melting at 65.3° , and giving on sulphonation the characteristic chloride melting at 117° when opaque (*Proc. Chem. Soc.*, 1890, 83). By the Sandmeyer process, it was converted into a chloronaphthalenedisulphonic acid, the chloride of which, $\text{Cl} \cdot \text{C}_{10}\text{H}_5 \cdot (\text{SO}_2\text{Cl})_2$, crystallised from a mixture of benzene and light petroleum in radiate groups of prismatic needles, and from acetic acid in small prisms, melting at 130° , which on distillation with phosphorus pentachloride gave 1:3:4'-trichloronaphthalene crystallising from alcohol in long slender flat needles melting at 103° .

When dry potassium 1:3- α -chloronaphthalenesulphonate is sulphonated under the conditions described in a previous note (*Proc. Chem. Soc.*, 1890, 131) by adding it to the theoretical quantity of sulphuric anhydride used in the form of 20 per cent anhydrosulphuric acid, and heating the warm mixture at 100° for an hour, it is converted into a chloronaphthalenedisulphonic acid identical with

that just described. No trace of an isomeric acid was detected. As in previous cases, details as to the composition of the salts, &c., are reserved for the complete paper.

It follows, therefore, that under the conditions described the disulphonic acids obtained both from the 1:3- α -amido- and the 1:3- α -chloro-monosulphonic acids have a corresponding constitution expressed by the symbols—



PHYSICAL SOCIETY.

Ordinary Meeting, January 24th, 1896.

Captain W. DE W. ABNEY, President, in the Chair.

MR. CAMPBELL SWINTON exhibited some Photographs which had been taken by Prof. Röntgen's method.

These included several of metal objects inside wooden and cardboard boxes, and a very clear and sharp photograph of the bones of the hand.

MR. E. SCOTT showed some Geometrical Instruments invented by himself and Signor Monticolo.

The instrument designed by Signor Monticolo is intended for drawing arcs of circles of such large radius that compasses cannot be employed. It can be used to trace arcs of circles of which the radii vary from 50 c.m. to infinity.

The second instrument exhibited was a modified form of hatchet planimeter which Mr. Scott has devised with a view of avoiding some of the defects of the ordinary form of instrument. Thus, to avoid the cutting of the paper, which occurs when the knife edge is sharp, and the side-slip which occurs when the knife edge is blunt, the author uses a wheel with a sharp edge. To avoid the inclination of the instrument to one side, which may easily occur with the ordinary form, a flat celluloid plate with a dot at the centre is used as the tracing point; this plate being kept pressed flat on the surface of the paper. A small wheel with a recording disc is attached, and may be used to measure the distance between the first and last position of the knife edge.

Mr. Scott also described a form of planimeter which he had invented, and in which the disc and cylinder movement is used to perform the integration.

MR. C. V. BOYS said that an instrument designed by Mr. Clarkson had been exhibited before the Royal Society which was capable of drawing arcs of circles of large radius. This instrument only drew an approximation to a circle, but the approximation was so close that it nowhere was more than the thickness of a thin ink line away from the truth. It would be interesting to hear from the author whether Signor Monticolo's instrument drew a rigorously exact circle or not. The upright position of the hatchet planimeter might be secured by using two wheels in place of one. The planimeter described was really a modified form of one he (Mr. Boys) had described before the Society in 1881.

MR. BLAKESLEY gave a short geometrical proof showing that the curve traced by Signor Monticolo's instrument was rigorously an arc of a circle. Mr. Blakesley also drew attention to the fact that the instrument in its present form cannot be used to trace the arc on both sides of the zero line.

DR. C. V. BURTON described an idea for an instrument for drawing circular arcs which had occurred to him, depending on the use of two wheels of different radii connected by an axle conveying a tracing point.

In the absence of the author, a paper by Prof. J. D.

EVERETT, on "*Resultant Tones*," was read by Dr. C. V. BURTON.

The author, after giving a short summary of the Helmholtz theory of the production of resultant tones, goes on to discuss his objections to this theory, and to elaborate a theory of his own. This theory depends on the consideration that if you analyse into a Fourier series a periodic curve which is compounded of two simple harmonic motions, of frequencies n and m , then only two terms are obtained. If, however, some error has been originally made in adding the two simple harmonic motions together, this error being repeated for each wave, then, in addition to the two terms of frequency n and m , there will be obtained, when the curve is analysed, a term of frequency f ; where f is the greatest common measure of n and m . This term of frequency f the author calls the common fundamental of the tones n and m . The "error" in the production of the compound curve, the author supposes to be produced during the transmission of the sound by the ossicles of the ear. In support of his theory the author finds that in the violin, where the sound-post, like the ossicles of the ear, transmits the vibrations from one portion of the instrument to another, it is easy by sounding two strings in conjunction to obtain combination tones which agree in frequency with those required by this theory. Thus, when the major sixth (3:5), the major second (8:9), or the minor seventh (5:9) are sounded, the fundamental (1) is clearly heard, and also felt by the hand holding the instrument. The author has also succeeded in picking out and strengthening this resultant tone by holding a Helmholtz resonator in contact with the body of the violin.

DR. C. V. BURTON, after explaining several portions of Prof. Everett's paper, said that he (Dr. Burton) considered that the author's view in many ways seemed to fit in with the observed facts better than the accepted theory, but still did not appear itself quite free from objection. Prof. Everett supposes that the first term in a Fourier series is always the most important, and although in most cases which occur in practice this may be so, it hardly seems legitimate to take this as a characteristic of a Fourier series.

The thanks of the Society having been given to Prof. Everett and Dr. Burton, the meeting adjourned to February 14th.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Fourth Ordinary Meeting, January 13th, 1896.

DR. J. E. MACKENZIE in the Chair.

MR. KERR read a paper on "*The Paraffin Industry*."

He mentioned that the industry is a comparatively modern one, and was founded by the late Dr. James Young, of Kelly. The Boghead mineral, originally used, was exhausted in 1862, and since that time the main source has been the bituminous shale lying under the coal formations. About two million tons of this mineral are mined annually in this country.

The lecturer went on to give a description of the process as carried out in the works of the Linlithgow Oil Co., Lim., near Linlithgow, to which there was an excursion of the Society during the summer.

In these works about 700 men are employed, of whom fully one-half are miners.

On an average, 550 tons of shale are brought to the surface each day.

From the mine-head, after being disintegrated in the "breaker," the shale is conveyed in hutches to the top of the retorts, into which it is tipped.

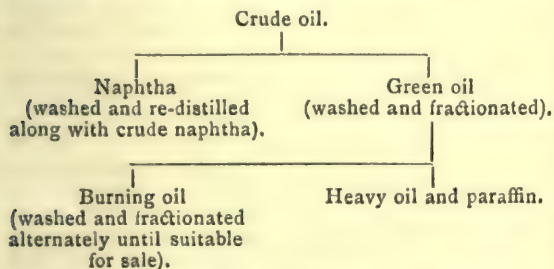
The retorts in use in the Linlithgow works are of the Young and Beilby type, having a re-distillation chamber in connection with each set of four. The coal-furnaces

are of brick-work, and are placed between the sets of retorts, two of them serving to heat eight shale retorts. Round these latter are the flues in which the gases from the furnaces are consumed.

From the shale are obtained directly:—The crude oil, ammonia water, and gases containing volatile hydrocarbons.

The crude oil yield depends on the form of retort and nature of the shale used, varying from 17 to 35 gallons per ton of shale. The ammoniacal liquor yields from 17 to 80 lbs. of ammonium sulphate, and the retort gases, when scrubbed, about $1\frac{1}{2}$ gallons of naphtha per ton of shale.

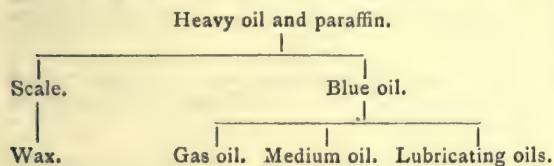
After being settled and separated from the ammonia liquor, the crude oil is put through a series of washings with acid and soda and fractional distillations.



The burning oils vary in gravity from 0.800 to 0.820. The flash-point in Scotch oils is never below 100° F., rarely below 110° F., while a large quantity of oil is imported from America flashing at or even below 73° F.

The heavy oil and paraffin is frozen and pressed. Solid paraffin (known as "scale" when in the crude state) is left in the filter presses, while blue oil passes through.

This latter undergoes further treatment with acid and soda, and is fractionated into gas and lubricating oils.



The lubricating oils are displacing vegetable ones for machinery, since they neither clog nor are liable to spontaneous combustion.

The paraffin scale, after further pressing, is purified by "sweating" out the oil and colouring-matters, and is then washed with bone-black, filtered, and run into cakes.

The lecturer then described the method of candle manufacture in some detail.

The paper was illustrated by diagrams and specimens of the products in various stages.

In the discussion which followed, the Chairman, and Messrs. Watson, Fairbairn, Smith, Lauder, and Gregory took part.

Mr. CLARKSON pointed out that when stearine is added to the wax in candle making, although the wax is rendered harder, the melting-point is lowered.

The meeting concluded with the usual votes of thanks.

The State of Sulphur in the Products of the Combustion of Coal-Gas.—In a series of experiments the proportion of sulphur in the products converted directly into sulphurous anhydride was found to be respectively 93, 89, 99, and 93 per cent of the total sulphur. Hence the authorities who maintain the direct formation of sulphuric acid are in error.—*Revue Universelle des Mines et de la Metallurgie*, xxxi., No. 1.

NOTICES OF BOOKS.

Notes on the Nebular Theory in Relation to Stellar, Solar, Planetary, Cometary, and Geological Phenomena. By WILLIAM FORD STANLEY, F.R.A.S., F.G.S., F.R. Met. Soc., M. Phys. Soc. London: Kegan Paul, Trench, Trübner, and Co. (Ltd.). 1895. 8vo., pp. 259.

FROM a first glance at the title of this work we were led to expect a discussion of the origin of the elements, and indeed of matter in general. As such researches, despite the protests of Positivism, have an intense fascination for minds who do not despair of the progress of Science, we opened it eagerly; but we at once found that there is here little to claim the attention of the chemist as such. Mr. Stanley has revised the celebrated nebular theory of Laplace, applying it to the sizes, the respective distances, and the temperature of the planets,—to the configuration of the earth's surface, to the glacial epoch, and other astronomical and geological phenomena. We find, indeed, that he accepts the concept of a *protyle*, and suggests the possibility of a number of elements much exceeding those which have been respectively isolated. The dissociation units, or *pneumites* as he terms them, must, he considers, be very much smaller than the atom, probably not exceeding 1-10,000th of its diameter. He thinks that atoms formed of pneumites of perfectly concordant period will be stable, such as gold. Atoms formed of pneumites partly of slightly discordant period will be unstable. Atoms may have concordant periods of vibration, though their pneumite composition may be partially discordant with other atoms. Matter formed of such concordant atoms with other atoms would have a tendency to associate in chemical combination or alloy, as nickel and cobalt, the two groups of the platinum metals, yttrium and didymium, &c. Here the author refers to the well-known address of Mr. Crookes to the Chemical Society in 1888.

Mr. Stanley, as we are not sorry to find, is unable to accept the brachychronology of Lord Kelvin, or the hypothesis of an earth solid and rigid to the centre. Nor does he admit of uniformly progressive cooling of the sun—a point of great weight in speculations on the cause of glacial epoch; but he has no doubt concerning the ultimate dismal fate of our planet, and the death of the "last man," from cold and hunger, in what is now the deepest part of the bed of the Pacific.

To astronomers and geologists the work will be suggestive reading.

Machinery and Appliances for Manufacturing Chemists. By JAMES C. SHEARS, Assoc. Inst. C.E. London: E. Marlborough and Co. 1895. 8vo., pp. 93.

THE selection and construction of apparatus for the various branches of manufacturing chemistry is now a matter of great importance, as a process which gives excellent results in the laboratory may, on a commercial scale, prove utterly useless for want of suitable mechanism. Hence the little work before us may be in many cases of great utility.

The general remarks on chemical factories speak of practical experience. Concerning the water-supply of such establishments, it may be added that its quality is of capital moment. The more closely it approaches distilled water the better. Hard waters, and such as contain iron, should on no account be used.

The author gives a comparative table of the value of different fuels, Welsh coal being taken as unity.

The subject of distillation has its painful side. According to the letter of the law, every apparatus for this purpose is still subject to an excise impost, however incapable it may be of serving for the manufacture of alcohol. Hence the exemption which chemists now practically enjoy is merely of courtesy, and not of right.

We regret to find that Mr. Shears has omitted auto-claves, which are indispensable for the production of coal-tar colours, and monte-jus. Perhaps, in the very probable case of a second edition being called for, he will introduce these subjects, and also the electric furnace, which is now doing such good service.

Bleaching and Calico Printing: a Practical Manual. By GEORGE DUERR, Director of the Bleaching, Dyeing, and Printing Department at the Accrington and Bacup Technical Schools, Chemist and Colourist of the Irwell Print-Works. Assisted by WILLIAM TURNBULL, of Turnbull and Stockdale (Ltd.). With Diagrams of upwards of 100 Dyed and Printed Patterns, designed to show various stages in the processes described. London: Griffin and Co. (Ltd.). 1896. 8vo., pp. 142.

THIS work, as the reader will perceive, does not extend to the bleaching and printing of tissues in general, but exclusively to cotton goods. Hence the list of mordants is reduced as compared with those necessary thirty or forty years ago. The extent to which coal-tar colours have superseded the natural dyes and pigments has acted in the same direction. The author admits that for general bleaching purposes nothing has yet been discovered preferable to the hypochlorites, some of which are from time to time advertised, under new names, as novel inventions.

We see that in the dunging process no arseniates are recommended—a step in the right direction. The same remark applies to the extract styles, in which arsenical and antimonial ingredients are no longer recommended, though they admit of beautiful effects being produced with the basic colouring-matters. We are glad to find the admission that artificial indigo is still not much used. It is a remarkable and unpleasant fact that for a "chrome yellow" that prepared by Bayer and Co. is directed to be used. Can we not make a satisfactory chrome yellow in Britain? The same applies to "brilliant yellow,"—i. e., cadmium sulphide. If, after all the labours of the syllabus constructors, we cannot produce such simple colours at home, something is in need of alteration.

The part taken by Read, Holliday, and Sons, in the production of diazo colours directly upon the tissue, is duly recognised.

Blood-albumen has of late been so much improved that egg-albumen is rarely used as a thickener, thus greatly cutting off a waste of human food.

In the removal of grit from colours prepared for printing there is still room for invention.

We question whether any of the coal-tar colours can be pronounced more brilliant than safflower and its extract carthamine.

The demands made on soaps by the printer and dyer are fully explained and justified.

The theory of colours is considered at some length. The author or authors (?) do not accept the modern theory of three primitive colours,—red, green, and violet,—but consider that they are practically three others, red, yellow, and blue.

Guide to the Determination of Molecular Weight according to Beckmann's Freezing- and Boiling-points Methods. (Anleitung zur Molekular gewichts bestimmung nach der Beckmannschen Gefrier- und Siedpunkts Methode).

THE author explains and illustrates Prof. Beckmann's two methods of ascertaining the molecular weights of substances by means of the freezing-point and the point of ebullition. He appends the caution that, in the former method, abnormal values may be produced by the joint crystallisation of the dissolved substance. In the ebullition method errors may occur if the substance is volatile, i. e., if its point of ebullition is not at least 150° higher than that of the solvent.

CORRESPONDENCE.

ACETIC ACID DISTILLATION.

To the Editor of the Chemical News.

SIR,—I shall feel obliged to any of my *confrères* experienced in acetic acid distillation from the commercial brown acetate of calcium, calculated as 68 per cent of acetate, distilled with hydrochloric acid of about sp. gr. 1.1599 (32.213 per cent), if they would give me commercially the yields of real acetic acid.

I wish to know the above through the chemical public with a view to some discussion.—I am, &c.,

P. L. ASLANOGLU.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 1, January 6, 1896.

M. Marey, the retiring President, gave the usual yearly notice of the condition of the Academy, the death of members and foreign associates during the past year, and the election of new members in their place.

The death-list includes Pasteur, Verneuil, and Larry. The academicians elected are Hautefeuille, Guignard, Lannelongue, and Carnot.

Two members have still to be elected; one for the section of Mineralogy, and one as a "free Academician." The foreign associates elected are:—Weierstrass, of Berlin; Frankland, of London; and Newcomb, of Washington.

Among the deceased correspondents we notice that Professor Huxley is described as "of Odessa." Prof. van Beneden is spoken of as deceased, and also as advanced from the rank of a correspondent to that of a foreign associate.

In the section of Anatomy and Zoology anti-evolutionism seems still predominant.

The Perpetual Secretary announced the death of J. Russell Hind, and F. Tisserand gave an account of the work of the late astronomer.

Action of Nitrogen Peroxide upon the Haloid Salts of Tin.—V. Thomas.—The author refers to the previous researches of Kullmann, Weber, and Hampe, on the action of the nitrogen oxides on the haloid salts of tin. He has resumed the study in a chloroformic solution of the compounds which are formed by the action of NO₂ upon all the haloid persalts of tin. With SnCl₄ the reaction is very brisk, producing a crystalline precipitate of the composition SnOCl₂·SnCl₄·N₂O₅. It is soluble in water, hygrometric, and if heated it is decomposed, yielding a crystalline sublimate. The action upon SnBr₄ yields a white powder, partially soluble in water with decomposition. On heating it is decomposed into stannic acid and nitrous vapour, with probably nitrogen oxybromide. The residue is stannic acid. With SnI₄ the reaction is more difficult. There is produced a voluminous precipitate of iodine. The white product, when free from iodine, is not crystalline and insoluble in water, by which it is not affected.

On a Method of the Decomposition of some Compounds having an Amide or a Bromide Function.—Oechsner de Coninck.—The author has submitted several aromatic derivatives to the action of Leconte's reagent. See *Comptes Rendus* (1895; Dec., 1896).

No. 2, January 13, 1896.

At the meeting of the Society, January 13th, Marcel Bertrand was elected a member of the Mineralogical Section, *vice* Pasteur, deceased.

A Photometric Standard with Acetylene.—J. Violle.—Acetylene, in the author's model, issues from a small conical orifice carrying with it the necessary quantity of air. It then penetrates, by a narrow aperture, into a tube where the mixture is effected, and which terminates with a bat's-wing burner made of steatite. The entire flame corresponds to more than 100 candles under the pressure of 0.30 metre of water. The consumption of ethylene is 58 litres per hour. We see that the illuminating power of acetylene is more than 20 times that of coal-gas burning in a Bengel burner (giving 1 carcel = 9.6 candles for 105 litres), and at least 6 times that of the same coal-gas for an Auer burner (giving 1 carcel for 30 litres).

Formation-Heat of some Compounds of Manganese.—H. Le Chatelier.—Metallic manganese evolves a rise of temperature of 164 cal. Manganese carbide yields 5.2 cal. Manganese protoxide evolves 45.4 cal. Manganese dioxide gives 63 cal. Manganese carbonate 13.8 cal. Manganese silicate 2.7 cal.

Crystalline Strontium and Calcium Iodides.—M. Tassilly.—A thermochemical paper, the chief novelty of which is an apparatus for drying the substances in a current of dry air deprived of carbonic acid.

On the Aldehyds Derivatives of the Isomeric Alcohols, $C_{10}H_{18}O$.—Ph. Barbier and L. Bouveault.

On the Multirotation of the Reductive Sugars and of Isodulcitol.—M. Tanret.—These two papers are not suitable for useful abstraction.

Journal für Praktische Chemie.
New Series, Nos. 8 and 9, 1895.

Communications from the Chemical Institute of the University of Kiel. Hydrazides and Azides of Organic Acids. Treatise V.—27. On Substituted Glycolic Esters and Glycol Hydrazid.—Th. Curtius.—The author, with the co-operation of M. Schwann, examines here the substituted glycolic esters from diazoacetic ester; that is, 1, glycolic ester; 2, phenylglycolic ester; 3, benzylglycolic ester; 4, ethylglycolic ester; 5, benzoylglycolic ester; 6, hippuryglycolic ester; 7, oxalylglycolic ethyl ester; 8, succinylglycolic ester; the action of hydrazinhydrate upon the substituted glycolic esters—that is, that of hippurylglycolic ester, oxalylglycolic ester, succinylglycolic ester, and benzylglycolic ester. The authors next examine glycolhydrazid, its fission in acid solution, its compounds with aldehyds and keto-substances, such as benzalglycolylhydrazin and its ortho- and para-modifications, acetophenon glycolylhydrazin, glycolhydrazinacetacetic ester, glycolhydrazid-anhydride, hydrazoglycolid and its hydrochloride. In Treatise VI. Th. Curtius discusses the behaviour of hydrazin hydrate with phthalic acid and maleic anhydride. Then follows an experimental examination of phthalic hydrazid, its potassium, sodium, and silver compounds, its behaviour with benzaldehyd, with the mineral acids, and with bromine; diacetyl phthalhydrazide, methylphthalhydrazide, phthalhydrazidacetic ester, and phthalhydrazidacetic acid, its ammonium and diammonium compounds. Then follow experiments on the reduction and oxidation of phthalhydrazid, the action of maleic anhydride upon hydrazin hydrate silver- and copper-amidomaleinimides, acetylamidomaleinimid, maleinhydrazid, hydrazin maleate, trimethylpyrazolin maleate, trimethylpyrazolin chloride, and picrate and hydrazorin fumorate.

Researches from the Laboratory of the University of Freiburg, in Breisgau.—These consist of a paper by

Ad. Claus on kyaphenin and some substituted benzonitriles; and a memoir by Claus and Alf. Ammelburg, on meta-ana-dichlorquinolin.

Contributions to our Knowledge of Anethol.—C. Hall.—These contributions consist of a paper by C. Hall and G. Gärtner, on the action of bromine upon anethol.

Oxidation Experiments, with some Derivatives obtained by the Action of Ortho- and Para-toluolsulphone Chloride upon Amidic Substances.—J. Träger and P. W. Uhlmann.—The authors have experimented on the anilides of ortho- and para-toluolsulphonic acid; on the condensation of para-toluolsulphon chloride and para-amidophenol; on oxidations of the condensation-products obtained in the experiment last-mentioned; the condensation of para-toluolsulphon chloride and ortho-amidophenol, with meta-amido phenol, and with phenylhydrazin.

The Benzene Nucleus.—W. Vaubel.—In this paper the author considers the solubility in water of some disubstituted products of benzene and the acetylation of aromatic amidosulpho acids.

A Correction.—C. Schall.—The author protests against an erroneous view in a notice of his "Determinations of Vapour Densities" (*Berichte*, xxiii., 919 and 1701), given as far back as 1890.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxi., No. 1.

Researches on the Relations between the Degree of Fusibility and the Composition of the Ash of Coal.—Eugene Prost.—The phosphoric anhydride in some kinds of coal reaches 2.02 per cent, whilst in others it is as low as 0.26, and in others again it exists merely as traces. The localities of the coals are not given.

Mounds of Coal-Ashes and the Hardness of Waters.—It is certain that coal-ashes rich in soluble compounds must increase the hardness of any waters with which they may come in contact. It is therefore important that the deposits of ashes from furnaces should be placed as remote as possible from wells, reservoirs, &c.

MISCELLANEOUS.

Prof. Röntgen, of Würzburg, after a Lecture which he had delivered on the Crookes vacuum tube, was invested with the Order of the Crown (Kronen Orden), second class.

Action of Nitric Oxide on Ferrous Chloride.—V. Thomas.—If into a perfectly dry glass tube, containing anhydrous ferric chloride, we pass a current of perfectly dry nitric oxide, there are formed, according to the temperatures, two distinct compounds of nitric oxide and ferric chloride. At the same time there are disengaged abundant yellowish brown fumes, of a substance which is deposited on the colder parts of the tube, and much resemble iron oxychlorides. If the temperature is raised, we see the appearance of white lamellæ of ferrous chloride. If these are allowed to cool in a current of the gas they take a fine red colour, and absorb nitric oxide. The yellowish brown substance has the composition Fe_2Cl_4NO . The red substance corresponds in its composition to the formula $5Fe_2Cl_4NO$.—*Bull. de la Soc. Chim. de Paris*.

ERRATUM.—P. 27, col. 2, line 25 from top, should read as follows:—“(b) Mercuric oxide, 3.5 grms.; glacial acetic acid, 20 c.c.; and water 100 c.c., are mixed together.”

MEETINGS FOR THE WEEK.

- MONDAY, Feb. 3rd.—Society of Arts, 8. (Cantor Lectures). "Alternate Current Transformers," by Dr. J. A. Fleming, F.R.S.
 — Medical, 8.30.
 — Society of Chemical Industry, 8. "Manufacture of Linoleum," by W. F. Reid, F.I.C.
- TUESDAY, 4th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.
 — Society of Arts, 8. "The Garden in relation to the House," by F. Inigo Thomas.
 — Institute of Civil Engineers, 8.
 — Pathological, 8.30.
- WEDNESDAY, 5th.—Society of Arts, 8. "The Mexican Drainage Canal," by F. H. Cheesewright, M.Inst.C.E.
 — Geological, 8.
- THURSDAY, 6th.—Royal, 4.30.
 — Royal Society Club, 6.30.
 — Royal Institution, 3. "Dante," by Philip H. Wicksteed, M.A.
 — Chemical, 8. "Molecular Weight and Formula of Phosphoric Anhydride and of Metaphosphoric Acid," by Prof. Tilden, F.R.S., and R. E. Barnett.
 — "Lead Tetracetate and the Plumbic Salts," by A. Hutchinson, M.A., Ph.D., and W. Pollard, B.A., Ph.D.
 — "An Improved Mode of Determining Urea by the Hypobromite Process," by A. H. Allen.
 — "An Examination of the Products obtained by the Dry Distillation of Bran with Lime," by W. F. Laycock, Ph.D.
 — "Luteolin," by A. G. Perkin.
- FRIDAY, 7th.—Royal Institution, 9. "Portrait Painting in its Historical Aspects," by the Hon. John Collier.
 — Geologists' Association, 7.30. (Anniversary).
 — Quekett Club, 8.
- SATURDAY, 8th.—Royal Institution, 3. "Realism and Idealism in Musical Art," by Prof. C. Hubert H. Parry, D.C.L., &c.

TO CORRESPONDENTS.

C, V.—Yes, to both questions.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1889.

CERTAIN PROPERTIES OF RÖNTGEN'S RAYS.

By JEAN PERRIN.

I WILL admit at once that I have had only very vague information drawn from the daily papers concerning Prof. Röntgen's discovery, and that I am still in ignorance as to the exact nature of his experiments.

However it may be, here are those which I have attempted.

I. I have first repeated that which constitutes the discovery: if we place, in presence of a Crookes's tube in activity, a photographic case charged and closed, on which are arranged different objects, and if in these develop the plate in the ordinary manner, we see appear the shadows of certain of these objects; something which emanates from the tube has impressed the plate through the interposed bodies. This is Röntgen's radiation.

These rays are not *kathode rays*; these latter cannot, in fact, issue from the vacuum tube except through a wall of some microns in thickness, whilst Röntgen's rays act easily out of a tube the side of which may have the thickness of 1 m.m.

II. I then collected some indications as to the degree of transparency of different substances.

Wood, paper, wax, paraffin, water, appeared very transparent, though the influence and thickness remained very distinct. Then come, arranged in the order of increasing opacity, coke, bone, ivory, spar, glass, quartz (either parallel or perpendicular to the axis), rock-salt, sulphur, iron, steel, copper, brass, mercury, lead. These results are still not numerous, and I cannot think of combining them by general law; still we may remark that the metals are in general less transparent than the substances, but have not the absolute opacity which they present for light. If, e.g., we superimpose three plates of iron, each of about 0.2 m.m. in thickness, opacity appears only in the region covered by all three plates.

III. I then made a rather rough experiment in order to find if the radiation is well-defined, or if it merely forms a diffused tuft; in a word, I have examined if its propagation is rectilinear.

To this end I placed before the tube two diaphragms of brass (which is opaque), at the distance of some centimetres, on a sensitive plate placed a little further. I obtained a very definite spot with an umbra and a penumbra, and the dimensions of this spot agree with the hypothesis of rectilinear propagation.

It is therefore possible to isolate definite pencils, the properties of which will be studied.

IV. I have attempted the reflection of a pencil of Röntgen's rays, defined by two slits of 0.5 m.m. at the distance of 4 c.m. The pencil fell upon a mirror of polished steel at an angle of 45°, whence after reflection it could fall upon a filled frame. After an hour's exposure I obtained absolutely no impression.

The experiment was repeated with a plate of flint-glass as a mirror. The exposure was prolonged for seven hours, but absolutely nothing was obtained.

V. I attempted the refraction of Röntgen's rays. In the lower half of the pencil, defined by the system of slits, I interposed first a prism of paraffin of 20°, and a prism of wax at 90°. The two parts of the pencil should give distinct images if refraction took place; but the two images were prolonged exactly, and we may affirm that if any deviation exists it is inferior to 1°.

VI. Continuing to seek for some properties of Röntgen's

rays capable of co-existing with a rectilinear propagation, I attempted to form diffraction fringes.

The active part of the tube was placed before a very narrow slit; at 5 c.m. further was placed a slit of 1 m.m., and at 10 c.m. further the frame fitted and closed. The exposure was continued for nine hours. I obtained an image with very distinct margins, on which no fringe was perceived.

I placed, exactly at the place of the former plate, a second sensitive plate, and operated this time with an open frame, so as to receive the green light issuing from the tube. After some minutes this light gave a silhouette, exactly superimposed on the former, but on which fringes were seen.

If, therefore, the phenomenon is periodic, the period is much lower than that of the green light employed.

It is well to observe that this experiment, made very accurately, proves the rectilinear propagation of Röntgen's rays. Around this property which they possess more strictly than light are grouped those mentioned in this paper.

VII. Lastly, being curious to see what practical interest might attach to the silhouettes obtained, I experimented on some living tissues, with the assistance of M. Oigny, preparator of zoology at the Ecole Normale of M. Mouton, an *attaché* of the Museum. We have the honour of presenting to the Academy two proofs which represent very faithfully the skeleton and some organs of a flat-fish (*Pleuronectes*) and of a frog.

M. Poincaré made the subjoined remarks:—Professor Röntgen has already recognised that the X rays are not refracted; he has experimented with prisms formed of different materials; on one occasion only he thought that he observed a slight deviation, corresponding to an index of 1.05; but this observation remains doubtful. He has likewise seen that the rays do not undergo a regular reflection, but he believes that they may experience an irregular and diffusive reflection.—*Comptes Rendus*, cxxii., p. 186.

THE KATHODE RAYS.

By JEAN PERRIN.

Two hypotheses have been proposed to explain the properties of the kathode rays.

Some authorities think, with Goldstein, Hertz, and Lenard, that this phenomenon is due, like light, to the vibrations of the ether, or even that it is light with a short wave-length. Others, Crookes and J. J. Thomson, consider that these rays are formed of matter charged negatively and travelling with great velocity. From a paper courteously forwarded us by the author, we learn that, according to his experiments, the facts observed do not easily agree with the theory which regards the kathode rays as ultra-violet light. On the contrary, they are in harmony with the theory which regards them as a material radiation.

ON THE UTILITY OF PHOTOGRAPHS IN HUMAN PATHOLOGY TAKEN BY MEANS OF THE X RAYS.

By MM. LANNELONGUE, BARTHELEMY, and OUDIN.

THE communication of Oudin and Barthelemy on this subject has led us to undertake some researches with a view of confirming our first results, and also of ascertaining what advantage we may obtain by the employment of Röntgen's rays.

We have therefore undertaken the researches, the first results of which I am about to lay before the Academy.

Our appliances are as yet imperfect, and we are aware of our own inexperience.

The first fact is that of an anatomical case. It is that of a thigh bone attacked with osteomyelitis. One of us has shown elsewhere that the malady known under this name is wrongly considered as a periostitis.

If this were true the bony alterations would have produced themselves from the surface to the centre of the bone. The photograph shows, on the contrary, that the surface of the bone is intact, whilst the internal layers are destroyed as far as half a m.m. from the surface.

Normally the compact osseous tissue, here reduced nearly to the thickness of a piece of paper, should have at least half a c.m. in thickness. This has allowed it to be traversed by the light, and this is the cause of the white spots remarked on the bone.

The second photograph is that of a tubercular affection of the first joint of the middle finger of the left hand.—*Comptes Rendus*, vol. cxxii., p. 159.

PROOFS OBTAINED BY MEANS OF RÖNTGEN'S PROCEDURES.

By H. DUFOUR.

THE hand of a child, the fingers of which were garnished with rings of brass and aluminium, yielded a proof in which we distinguish the projection of the rings, the outline of the skin, the structure of the bones, and in particular the incomplete ossification of the last joint of the little finger.

The photograph of a frog permits us to distinguish the bones of the pelvis of the limbs, and to some extent those of the head.

The proof of a trough with parallel sides partly filled with blood, showed merely a scarcely perceptible difference of intensity between the empty portion and that occupied by the liquid.

Ch. V. Zenger addressed a note regarding the recent experiments of Professor Röntgen.

The author recalls attention to his own communications made to the Academy of Sciences in February and August, 1886; the photograph of Mont Blanc which he obtained by night at the distance of 80 kilometres. He also drew attention to the researches of Hittorf, Hertz, and Ayrton, who have shown the permeability of plates of sulphur, vulcanite, plaster, &c. According to him the kathode radiation is merely the invisible ultra-violet radiation produced in the rarefied space of the Crookes tubes, and it has been already demonstrated that it is arrested by metallic plates. These radiations can develop fluorescence and phosphorescence in bodies which are opaque to the radiations of greater wavelengths.—*Comptes Rendus*, vol. cxxii., p. 213.

LUTEOL: A NEW INDICATOR.

By W. AUTENRIETH.

THIS substance is oxychloridiphenylquinoxalin, and has received the above name because it is a phenol, and takes in contact with alkalis an intense yellow colour. For its preparation we heat 1 mol. ethoxyphenylendiamine with 1 mol. benzil to ebullition, in an alcoholic solution. We thus obtain a crystalline precipitate of ethoxyphenylquinoxaline. This substance, fusible at 150°, is recrystallised from alcohol, and, heated with phosphorus pentachloride to 70° to 90°, in a paraffin bath, when by atoms chlorine enters into combination, whilst phosphorus trichloride and hydrochloric acid distil over. The ethoxychloridiphenylquinoxalin is then heated with hydrochloric acid to 180° to 200°, in a sealed tube, when alkyl is split off in the form of ethylen-chloride. The substance thus obtained is repeatedly re-crystallised from alcohol.

The fine, woolly, yellowish needles melt at 246°. At higher temperatures they sublime without decomposition. Luteol is insoluble in water, sparingly soluble in cold alcohol, but readily soluble in hot alcohol and in ether. Concentrated sulphuric acid dissolves luteol with a red colour, but it is re-precipitated by water. In concentrated hydrochloric acid it is sparingly soluble, but perfectly insoluble in the same acid if dilute. Alkalies dissolve it readily with a yellow colour. Luteol expels carbonic acid from the carbonates, and the acid character of the phenol is much increased by the introduction of an atom of chlorine. The sensibility of the change of colour is very great. If we add a drop of dilute soda-lye to 1 litre of water, and take 5 to 10 c.c. of the liquid, it is turned very distinctly yellow by the addition of a few drops of an alcoholic solution of luteol. Hence its sensitiveness is very decidedly greater than that of phenolphthalein and litmus. As compared with phenolphthalein it has the advantage of being applicable in presence of ammonia. It has the advantage over litmus because no intermediate colours appear in the change.—*Zeitschrift für Analytische Chemie*, xxxv., p. 68.

DIRECT COMBINATION OF THE NITROGEN OF THE ATMOSPHERE TO METALS IN THE STATE OF MAGNESIUM, ALUMINIUM, IRON, COPPER, &c., NITRIDES.

By A. ROSSEL.

IN the researches conducted for fixing the nitrogen of atmospheric air, several savants have succeeded in combining, in small proportions, this element, which in general possesses a very feeble activity.

James Pellat Rickman, in 1878, described an apparatus which rendered it possible to combine small quantities of nitrogen by heating coke with a fixed base in contact with air. Spongy platinum at high temperatures converts a small quantity of the nitrogen of the air into nitrous products, but in these two cases no analysis shows the exact figures.

Wigled and Geuther, in a remarkable investigation, demonstrated the affinity of magnesium for pure nitrogen, and described for the first time the compound Mg_3N_2 , which has recently played an important part in the discovery of argon by Lord Rayleigh and Prof. Ramsay.

M. Mallet has observed that magnesium, when burning slowly in air, yields not merely magnesium oxide, but a grey powder composed of magnesium and nitrogen.

M. Méry, of Zurich, has verified this fact, and found that, on heating magnesium to redness in a very weak current of air, there are formed small quantities of nitrogenous product.

Finally, C. Hinkler has shown that, on preventing the rapid oxidation of magnesium in air, by mixing it with magnesia there is formed a larger proportion of magnesium nitride.

In some studies on the reductive power of magnesium and aluminium, with which I have reduced at dull redness the metaphosphates which give off their phosphorus in a pure state, I have ascertained that there are formed secondary products containing small quantities of combined nitrogen. But whilst studying the important researches of H. Moissan, I came upon the most curious reaction concerning the combination of the nitrogen of atmospheric air in presence of oxygen.

In his work on the properties of calcium carbide, Moissan has shown that at high temperatures the metals have no action upon calcium carbide.

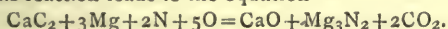
In concert with Léon Frank, I have found that it is not alike when we heat pulverised calcium carbide in powder with pulverised magnesium in a porcelain crucible, or in a tube in which there is a free circulation of atmo-

spheric air at the temperature of dull redness. The reaction takes place in a regular manner if we place in layers pulverised calcium carbide, and magnesium finely powdered, in a porcelain crucible.

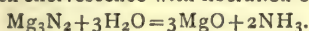
On heating the open crucible with the flame of a Bunsen burner, there soon appears a flame produced by the combustion of the carbon of the carbide, which gives rise to carbonic acid, and the calcium burns, producing calcium oxide. At this moment there ensues a lively incandescence, and, after cooling, the magnesium is almost totally converted into magnesium nitride.

The analysis of this product, which can be mechanically separated from the calcium, leads to the formula Mg_3N_2 ; the mixture of the residue in the crucible contains up to 23 per cent of nitrogen taken from the atmospheric air.

This reaction leads to the equation—



On mixing the contents of the crucible with water, there ensues a brisk effervescence with liberation of ammonia—



Aluminium, zinc, iron, and even copper, if mixed in fine powder with calcium carbide and heated in the air, give similar reactions.

There are formed nitrogenous products decomposable by water, and more easily by dilute caustic potassa.

These reactions, as M. Moissan has pointed out, are an additional proof that at the epoch of the formation of the earliest geological strata nitrogen did not exist in the free state, but in combination with metals.—*Comptes Rendus*, cxxi., p. 941.

THE SIZE OF ATOMS.

By HAROLD A. WILSON, Senior Akroyd Scholar,
The Yorkshire College, Leeds.

THE estimate of atomic dimensions depending on the surface energy of water and its latent heat of evaporation is well known. A quantity of water is supposed to be drawn out into a film of such an area that the work done in extending it is equal to its latent heat of evaporation. Take one gm. of water; then if A is the area required, we have $2A \times 86 = 600 \times 42 \times 10^6$; for 86 = the number of ergs per sq. c.m. of water surface at $0^\circ C.$, and 600 = the latent heat of evaporation of 1 gm. of water at $0^\circ C.$, therefore,—

$$A = 1.5 \times 10^8 \text{ sq. c.m.}$$

The thickness of the film is, therefore,—

$$\frac{1}{A} = 0.7 \times 10^{-8} \text{ c.m.,}$$

and this is taken as an approximation to the diameter of a molecule of water.

The data employed in the above calculation may be used to estimate the diameter of a molecule of water in another way, which, however, leads to a result of the same order of magnitude.

The pressure inside a bubble is given by the formula—

$$P = \frac{4T}{R};$$

where T = surface-tension of the water, and R = radius of the bubble. Suppose a bubble so small that the pressure in it is just double the internal pressure in water due to the attraction between the molecules; then its radius may be taken as an estimate of the diameter of the molecule (*i.e.*, the mean distance between the centres of the molecules). For if we suppose such a bubble, consisting of molecules of water only, to be submerged in water, then as the water molecules close round it its equilibrium will not be disturbed, because the pressure in it is already double that in the interior of the water, so that the space

within it will evidently be no greater than that usually between the molecules of the water.

The internal pressure in water is 1.3×10^{10} dynes per sq. c.m., as usually calculated thus:—The work required to bring a gm. of water into a water surface is put equal to half the latent heat of evaporation. This gives—

$$(p_1 - p_2)v = \frac{1}{2} \times 600 \times 42 \times 10^6 \text{ ergs;}$$

where p_2 = internal pressure,

p_1 = pressure in the surface = one atmosphere,
 v = volume of 1 gm. of water.

$$\therefore p_2 = \frac{1}{2} \times 600 \times 42 \times 10^6 = 1.3 \times 10^{10}.$$

For the radius of the small bubble then—

$$\frac{4T}{R} = 1.3 \times 10^{10} \times 2,$$

$$\therefore R = \frac{4 \times 86}{1.3 \times 10^{10} \times 2} = 1.3 \times 10^{-8} \text{ c.m.}$$

Surrounding a bubble with water of course halves the pressure in it since it destroys one surface, and therefore the pressure in the bubble is taken as being double that in the water.

The above may be more simply expressed as follows:—

The pressure in a spherical air bubble under water is given by $\frac{2T}{R}$. Now, consider the molecules in a liquid,

they are believed to be some distance apart, and the cavities between them may be supposed to have an average radius equal to their distance apart or diameter as above defined. Supposing the formula just given to apply to these cavities, we get $\frac{2T}{R} = p_2$, as before.

An estimate of the diameter of a molecule may also be obtained by considering the diminution of vapour pressure which occurs when a water surface is curved. The effect of curving the surface is to slightly more completely surround any molecule in the surface with other molecules. This increases the work necessary to force a molecule out, and so diminishes the average velocity of the molecules which escape. Assuming as a rough approximation that, with a spherical surface, the resistance to an escaping molecule is proportional to the angle, in a plane perpendicular to the surface of the liquid, subtended by the nearest other molecules when the molecule is at the surface we get—

$$\frac{\alpha}{\pi} = \frac{p_2 - p_1}{p_2};$$

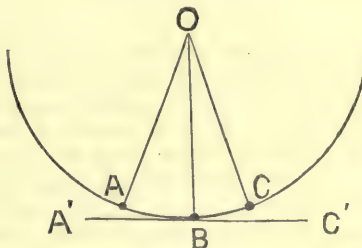
where $\pi + \alpha$ = the angle just mentioned,

p_2 = pressure with concave surface,

p_1 = pressure with plane surface.

Let $A B C$ be three molecules in the surface, and O the centre of the sphere formed by the surface, then—

$$\angle C'BC = \frac{1}{2}\alpha = \angle BOC;$$



but—

$$BC = OC \times \angle BOC = OC \times \frac{\alpha}{2} =$$

the distance between the molecules. Let $OC=r$, and the distance between the molecules d , then $d=\frac{1}{2}r\alpha$; but

$$\alpha = \pi \cdot \frac{p_2 - p_1}{p_2} \therefore d = \frac{\pi r}{2} \cdot \frac{p_2 - p_1}{p_2}.$$

But we have that—

$$\frac{p_2 - p_1}{p_2} = \frac{2T\sigma}{p_2 r \rho};$$

where σ = density of the water vapour,
and ρ = density of the water,

$$\therefore d = \frac{\pi T \sigma}{p_2 \rho}.$$

At 0° C. this gives roughly, since then,—

$$\sigma = \frac{5 \text{ gm.}}{10^6 \text{ c.m.}^3} \text{ and } p_2 = 6 \times 10^3 \frac{\text{dynes}}{\text{c.m.}^2}$$

$$d = \frac{3.1 \times 86 \times 5}{6 \times 10^3 \times 10^6} = \frac{2.2}{10^7} \text{ c.m.}$$

We should expect this result to be large, because it is evident that the resistance to an escaping molecule will increase less rapidly than the angle $\pi + \alpha$ when α is small. Considering the nature of the assumptions made in the above estimations, the results are remarkably concordant, and seem to me to afford some additional confirmation of the limits 10^{-8} to 10^{-7} c.m. for the diameter of a molecule of water.

ON THE PRESENCE OF SODIUM IN ALUMINIUM PREPARED BY ELECTROLYSIS.

By HENRI MOISSAN.

THE experimentalists who have occupied themselves with the properties of aluminium have often arrived at contradictory results. It has been the same when, on account of its low specific gravity, some countries have tried to use it for the manufacture of articles for the small equipment of infantry, such as drinking-cups. Sometimes the metal has behaved well, and shown properties which have caused its use to be advocated, but sometimes, on the contrary, its employment has led many to disappointment.

These difficulties depend on the difference of composition of industrial aluminium. We have already shown (*Comptes Rendus*, cxix., p. 12) that the metal may contain nitrogen and carbon, and that under these conditions its properties are remarkably modified. Its breaking and extension-weight decrease rapidly. Having had the opportunity of analysing aluminium obtained from the three great works at present established at La Praz (France), Neuhausen (Switzerland), and Pittsburg (United States), we have recognised a new impurity which seems to have a great importance as regards the preservation of the metal. We refer to the presence of sodium in industrial aluminium.

We may demonstrate the existence of sodium in some aluminums in the following manner:—We take 250 grms. of filings carefully prepared, which are placed in an aluminium bottle along with 300 c.c. of distilled water obtained in a metal still. The mixture was then left to itself for two weeks, heating it to ebullition every day. It was then thrown upon a filter, washed with boiling water,* and the filtrate, which is slightly alkaline, is evaporated to dryness in a platinum capsule. It is heated to dull redness, when the mass turns brown. We add pure hydrochloric acid diluted with water, when there takes place a distinct escape of carbonic acid. The liquid is again evaporated to dryness and heated to about 300° to expel any excess of hydrochloric acid, when we obtain a residue having all the characters of sodium chloride. We take

up the residue in water and determine the chlorine as silver chloride. From the weight of this latter compound we deduce the quantity of sodium removed by water from the aluminium filings.

When making the complete analysis of the metal we have found sodium in a number of specimens of aluminium. The proportion of sodium varies between 0.1 and 0.3 per cent. An aluminium prepared some time ago by the firm of Bernard contained 0.42 per cent.

When an aluminium contains a small quantity of sodium it is attacked by cold water at first slowly, but then the action proceeds with increasing intensity. In fact, if a small volume of water, not renewed, exists in presence of a leaf of such an aluminium, we see at first a slight layer of alumina forming upon the metal. Some days afterwards the liquid has an alkaline reaction with litmus paper. After this the reaction becomes more rapid. At every point where the aluminium contains sodium there is produced a little alkali, which reacts upon the metal so as to form an aluminate. This sodium aluminate is then dissociated by water with a deposition of alumina and a formation of soda, and when the liquid is slightly alkaline we understand how the decomposition becomes much more active.

The alloys which we may prepare with an aluminium will therefore possess quite different properties according as they contain or do not contain a small quantity of sodium.

The presence of sodium in industrial aluminium shows that the electrolysis of the mixture of cryolite and alumina gives rise to a number of secondary reactions in which the sodium may play a different part according to the composition of the bath and the intensity of the current.

It is thus that M. Riche, in a study of the alloys of aluminium and tin, has shown that these alloys decompose water at the ordinary temperature (*Journal de Pharmacie*, Series 6, vol. i., p. 5). I have succeeded in forming an alloy with 6 per cent of tin containing aluminium quite free from sodium, and under these conditions, after remaining two months in common water, the metal became spotted in several places, yielding small efflorescences of alumina, but not producing any escape of gas. My aluminium free from sodium was alloyed with 6 per cent of tin, avoiding the action of nitrogen and of the furnace gases, for M. Franck has proved that at a red heat aluminium decomposes carbonic acid, and even carbon monoxide. We thus obtain an alloy which, if rolled under a strong pressure, gave—

Tempered.—Resistance, 17.6; elasticity, 8.20; extension, 20.

Compressed.—Resistance, 23.43; elasticity, 22.90; extension, 6.

A leaf of this metal was divided into two parts. The first part was placed in Seine water, which was aerated daily by agitation. The second part was placed in a beaker of Bohemian glass in Seine water covered with a layer of oil several c.m. in thickness. The mean temperature of the laboratory was close upon 20° . The experiment was commenced on September 30, and was continued for two months. In this time the aluminium was covered with white efflorescence. It was spotted over almost its entire surface, but in neither case no bubble of hydrogen escaped. The specimen in the agitated water was oxidised the more rapidly.

This experiment was made only with an alloy containing a low proportion of tin. M. Riche has shown that with high proportions the decomposition of water becomes very active, and has thus established the reason which makes us reject every attempt at soldering with an alloy containing tin.

Aluminium is a metal which, if carefully tempered, works very well by means of rolling or stamping.

M. Riche informs me also that he has detected the presence of sodium in some samples of aluminium.

M. Meissonier, Chief Pharmacist at the Military

* In this experiment we often obtain a small quantity of soluble alumina, analogous doubtless to colloidal alumina which has passed through the filter and which is then precipitated.

Hospital of Saint Martin, who has undertaken prolonged researches on this subject, has even met with a sample of aluminium containing 4 per cent of sodium.

There is another important point on which we must insist regarding alloys of aluminium, those especially of copper. Every alloy which is not homogeneous is very difficult of preservation.

Dumas, in his memoir on the equivalent of aluminium, insisted on the non-homogeneity of aluminium prepared by the procedure of Deville.

We have had the opportunity of ascertaining, in moulded articles, the bad effects of a want of homogeneity. If we leave distilled water in such a vessel, we see in about a fortnight the appearance of small white spots of hydrated alumina. Each spot is surrounded with a brilliant halo, it continues to increase, and if we cut off the part attacked and remove the hydrated alumina, we generally distinguish with the microscope a small particle of carbon or of some other substance which has formed an element of a galvanic couple, and which has disaggregated the metal over a greater or smaller surface. If, instead of letting the water remain on this non-homogeneous aluminium, we leave on the surface a saturated solution of sodium chloride, the phenomenon is intensified, and each particle of carbon produces an attack of the aluminium foil sufficient to perforate it.

This formation of small battery elements over the surface of the aluminium is the chief cause of the deterioration of the metal.

On the other hand, with a metal quite homogeneous, containing neither nitrogen, carbon, nor sodium, there is no point of attack, and the water which has remained upon the metal retains all its clearness and contains no alumina.

The same phenomena appears with alcohol diluted with water, e.g., rum, and in case of aluminium of bad quality it explains the attack of certain vessels—an attack which sometimes takes place with very great energy.

I must remark, in conclusion, that aluminium, having a great disposition to form couples with every other metal, should never be used except alone.

A particle of iron or brass, on contact with aluminium, will always in a short time effect the oxidation of the metal and its conversion into alumina. All industrialists who have had to operate upon large surfaces of aluminium have observed, at their own expense, the generality of this decomposition.

In this research, conducted from a chemical point of view, we have not needed to insist on the importance of tempering in rolling and stamping aluminium. Without this precaution, the metal easily breaks and becomes unfit for any use.—*Comptes Rendus*, cxxi., p. 794.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, *Metropolis Water Act*, 1871.

London, January 10th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Dec. 2nd to Dec. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Com-

bustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined all were recorded as clear, bright, and well filtered.

The rainfall at Oxford during the month has been 2'08 inches, as against 2'10 inches, the average for the past 25 years; this shows a slight decrease, viz., 0'02 inch as compared with the average.

The rainfall for the year 1895 is detailed in the following table:—

	Actual fall.	Mean of 25 years.	Deficiency.	Excess.
January.. ..	2'60	2'26	—	0'34
February	0'21	1'92	1'71	—
March	1'46	1'59	0'13	—
April	1'78	1'78	—	—
May	0'16	1'95	1'79	—
June	1'12	2'21	1'09	—
July	3'41	2'58	—	0'83
August	2'28	2'24	—	0'04
September	0'57	2'66	2'09	—
October	2'85	2'56	—	0'29
November	4'17	2'31	—	1'86
December	2'08	2'10	0'02	—
	22'69	26'16	6'83	3'36

There is thus a deficiency of 3'47 inches, which has chiefly occurred during the months of February, May, June, and September.

Our bacteriological examinations for the month of December give the following numbers of colonies per c.c.

	Colonies per c.c.
Thames water, unfiltered	3259
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	110
Ditto ditto lowest	46
Ditto ditto mean	74
New River water, unfiltered	3933
New River water, from the Company's clear water well	65
River Lea water, unfiltered	3610
River Lea water from the East London Company's clear water well	64

These results show that the filtering arrangements of the Companies are highly satisfactory.

All the samples of water examined during the course of the past month gave satisfactory results; the amount of organic carbon shows a diminution, as compared with last year's report for the same period.

On the whole, during the course of the year, the London water supply has improved in quality.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

Melting- and Solidification-points of some Acids of the Fatty Series.—G. Massol.—The author has examined the propionic, valerianic (normal), isobutyric, and isovalerianic acids. They present distinctly the phenomena of superfusion; normal valerianic acid offering the greatest resistance to solidification. Of all the normal fatty acids at present known, valerianic acid melts at the lowest temperature (−58'5°). Among the abnormal, it is the isobutyric acid (−79°).—*Bull. de la Soc. Chim. de Paris*.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 52.)

CHAPTER V.

CHEMICAL RESEARCHES ON CARBONATE, OXALATE, SULPHATE, AND CHLORIDE OF CALCIUM.

SOME considerable time ago I tried to determine the atomic weight of calcium. I did not publish these researches, on account of the want of concordance in the results. At that time I tried to prepare some carbonate of calcium, both from chloride and pure nitrate, to compare its combining ratio with oxide of calcium, with that of Iceland spar. I found then that precipitated carbonate, and the same carbonate dissolved in water charged with carbonic acid, both retained water, a fact which is now generally known; besides this, I found that, when taking count of the water, carbonate which had been dissolved in water charged with carbonic acid, left—on calcination, in a platinum boat, put in a porcelain tube, traversed by a current of pure air—less oxide of calcium than the carbonate precipitated by sesqui-carbonate of ammonium, and also than the purest Iceland spar.

The atomic weight of calcium, as deduced from the artificial carbonate when re-dissolved in water containing carbonic acid, is nevertheless slightly greater than the figure required on Prout's hypothesis. The researches I have undertaken during the last few years have acquainted me with the difference in the composition of the calcic carbonates I prepared. I effected the decomposition of chloride and nitrate of calcium in glass vessels, by sesqui-carbonate of ammonium. It was by this means that I took up silicon and sodium from the glass, and combined it with the calcic carbonate formed. Having kept part of the salts made at that time, I was able to detect the presence of silica, not only in the carbonate precipitated directly, but also in the carbonate re-dissolved in water charged with carbonic acid.

All these researches had to be taken up again. The details into which I have entered will enable any one who desires to determine the atomic weight of calcium, to procure an oxide of this metal which I believe to be pure.

To satisfy myself of the identity of the calcic oxide, I had resource, successively, to the following natural or artificial compounds of calcium:—Colourless and transparent calc-spar and arragonite,—white marble,—and artificial oxalate, sulphate, and carbonate, made from nitrate which was prepared from Iceland spar. I submitted the calc-spar, arragonite, and white marble to the same treatment, to eliminate foreign bodies from them. I found silica, sodium, iron, and manganese in them all; traces of lithium, but neither strontium nor barium, in the Iceland spar; traces of lithium and magnesium, a notable quantity of strontium, but *not a trace of barium*, in the arragonite; and in the white marble, also, lithium, magnesium, and strontium, *without barium*.

Of all these foreign matters the elimination of sodium and strontium alone presented any difficulty.

Treatment of Iceland Spar.—Before commencing to separate the silica in a platinum vessel, which was sensibly attacked by melted nitrate of calcium, I had to effect the solution of the calcic carbonate by means of dilute hydrochloric acid, taking care to leave a small quantity undissolved. The chloride solution was boiled, in order to drive off the excess of carbonic acid, and then separated from the excess of carbonate used. Into the boiling liquid was poured, until it gave a decided alkaline reaction, some milk of lime reduced from oxide of calcium, which was made by calcining Iceland spar in a platinum vessel. After cooling it, the chloride solution was filtered; pure sal ammoniac was then added, it was evaporated to dryness in a platinum retort, and the residue was heated till

it gave off an abundance of chloride of ammonium fumes, the only method known to me for eliminating silica, the quantity of which was from 1-7000th to 1-8000th of the weight of Iceland spar.

The chloride of calcium, which still contained chloride of ammonium, was dissolved in water, and the solution, having been left to settle, was filtered to separate the free silica. The filter-paper used had been washed with very dilute hydrofluoric and hydrochloric acids, and then with pure water.

I twice evaporated the solution of chloride of calcium to dryness, raising the temperature high enough to volatilise each time part of the chloride of ammonium dissolved in the water on the first occasion; the absolute clearness of the liquid being doubtful, I filtered it. The second solution was perfectly clear. After being filtered again, it was diluted with as much pure water as the platinum vessels would hold, and gradually poured into a super-saturated solution of sesqui-carbonate of ammonium, which was both made and kept in a large platinum vessel under a bell-jar. After twelve hours' rest the supernatant liquid was decanted, the carbonate of calcium was put into a large covered platinum retort, and I washed the precipitate with cold water by decantation, using each time a quantity of pure water double the apparent volume of the carbonate. Fifteen washings with cold water were required to yield a decanted liquid which did not turn red litmus-paper blue. When this stage was reached, the washings still sensibly clouded an acid solution of nitrate of silver.

The washing was done by keeping the precipitate in suspension in boiling water, which was renewed until the liquid, having settled and been poured off, no longer clouded an acid solution of nitrate of silver. Twenty washings in boiling water were required to reach this stage. The carbonate was then dried in the same vessel.

Whenever I used the retort I took care to put on its lid, to prevent the dust of the air from falling into it.

I submitted the carbonate derived respectively from Iceland spar, arragonite, and white marble, to the following investigation:—

Carbonate from calc-spar, when taken straight from the retort on a recently heated platinum dish, turned an oxy-hydrogen blowpipe very slightly yellow. After heating it for fifteen minutes, during which time the surface of the thick coat of oxide was being renewed, spectrum analysis did not show the sodium spectrum more strongly than it could be seen in a blowpipe burning in the surrounding air.

The spectrum of calcium is described in the next chapter. This oxide, when heated to the fusing-point of iridium, does not show, after it has been reduced by volatilisation to the one-hundredth of its original mass, any trace of the spectra of lithium, strontium, or barium.

As regards sodium, the carbonates derived from arragonite and white marble behave exactly like that derived from calc-spar. On heating to a sufficiently high temperature, and maintaining it for some time, the resulting oxide easily frees itself from sodium. But it is necessary to heat the oxide of arragonite to the fusing-point of platinum, and the oxide of white marble to the fusing-point of iridium, in order to see the characteristic lines of strontium with the calcium spectrum. These experiments enabled me to prove with certainty the double influence of mass and temperature on the appearance or non-appearance of the spectrum of metals present.

I have not seen the spectrum of lithium in the vapour of the oxides of calcium from calc-spar, arragonite, and white marble. I have only found traces of lithium in the filtrates of chlorides made by means of bicarbonate of ammonium. All these liquids contain chloride of sodium. I was unable to detect the presence of chloride of potassium.

Although carbonate of calcium derived from Iceland spar showed no trace of the characteristic strontium lines, nevertheless I submitted it, as well as the carbonates ob-

tained from arragonite and white marble, to a similar treatment, to separate from it the strontium it might contain. For this purpose I followed Stromeyer's method.

I dissolved the carbonate, which had been precipitated and washed in pure nitric acid, in a platinum vessel. The solution was quickly evaporated down to a syrupy consistency, and the nitrate was then completely dried by putting the covered platinum retort into an air-bath, heated to between 150° and 170° .

Unless the dehydration is performed with the greatest care, the resulting salt is very basic, and it attacks the platinum, colouring the nitrate yellow. By some preliminary experiments I satisfied myself that, when the nitrate contains the least trace of water, absolute alcohol, when dissolving it, takes up strontium that cannot be precipitated by the addition of anhydrous ether. There is no question as to which is the lesser evil.

The dehydration being finished, the nitrate was taken up with the least possible quantity of absolute alcohol, and the cloudy solution was poured into a glass flask with a ground-glass stopper, and anhydrous ether added until the nitrate of calcium was precipitated. After the liquid had cleared, the flask containing it was put into a freezing mixture of sea-salt and ice. The liquid, becoming clouded afresh, was left in the freezing mixture until it became quite clear once more.

The clear and colourless supernatant liquid was most carefully decanted, so as not to disturb the precipitate, and it was filtered through a purified filter-paper, in a covered platinum funnel, and evaporated on a bath in a platinum vessel covered by a funnel larger than itself.

The deposit at the bottom of the flask was taken up by a mixture of equal volumes of absolute alcohol and ether, and poured into the filter used for filtering the bulk of the liquid. The etherised alcohol used to exhaust the insoluble mass was entirely separated.

I carefully examined the residue left by the nitrate of calcium made from Iceland spar, arragonite, and marble. The results I arrived at were as follows:—

The granular residue left, after treating spar, consisted entirely of basic nitrate of calcium, with traces of platinate of calcium, but no trace of nitrate of strontium. In fact, its oxide, when heated in an oxy-hydrogen blowpipe to the fusing-point of sodium, showed persistently and exclusively the calcium spectrum.

The granular residue left, after treating arragonite, consisted of a mixture of basic nitrate of calcium, slightly tinted yellow by platinate of calcium, and a noticeable amount of nitrate of strontium, recognisable in an oxyhydrogen blowpipe when the mixture of oxides is only treated to the fusing-point of platinum.

The granular residue left, after treating white marble, also consisted of a mixture of basic nitrate of calcium and nitrate of strontium, tinted by traces of platinate of calcium. The nitrate of strontium was very considerably less in quantity than in the arragonite.

Having found no trace of strontium in the nitrate of calcium from the Iceland spar used, I used it for preparing carbonate, oxalate, and sulphate of calcium, for the purpose of satisfying myself as to the identity of the oxide of calcium made from these salts. I shall return later on to this subject.

The solution of nitrate of calcium derived from arragonite and marble, from which the strontium had been eliminated as described above, was evaporated afresh in the platinum retort, and the residue most carefully dehydrated. I then repeated the whole treatment of the dried nitrate and the residue, with alcohol and anhydrous ether.

I found, beyond a doubt, the presence of strontium, but in a very small quantity, in the residue left by the nitrate derived from arragonite. I only found basic nitrate of calcium, tinted yellow by platinate of calcium, in the residue left by the nitrate derived from marble.

The solution of nitrate from arragonite was evaporated a third time, and the salt, when dried and entirely dehy-

drated, was again treated with etherised absolute alcohol. I was not able to detect, in the residue left by this third treatment, the presence of the slightest trace of strontium, when testing for it in an oxyhydrogen blowpipe at the fusing-point of iridium.

Thus, although nitrate of strontium may not be absolutely insoluble in an alcoholic and etherised solution of nitrate of calcium, as is easily ascertained, we can, nevertheless, eliminate the strontium, thanks probably to the formation of a basic nitrate of calcium, which is quite insoluble in etherised alcohol.

The nitrates of calcium from arragonite and marble, when freed from strontium, were converted into carbonate, just as I have described for the nitrate derived from Iceland spar.

I purified about 350 grms. of colourless and transparent Iceland spar.

The nitrate made by the method described above was divided into three parts, A, B, and C. The first, A, was converted into carbonate; the second, B, into oxalate; and the third, C, into sulphate, and partially into carbonate.

I effected the conversion into carbonate in platinum vessels, by means of sesqui-carbonate of ammonium, as I have described above, with reference to chloride of calcium. The carbonate was washed and dried in the same way, and with the same care. It is useless to repeat these details. I converted the second third, B, into oxalate, using an oxalate of ammonium which had been repeatedly crystallised in a platinum dish until 10 grms. of it, after calcining, left no weighable residue, which takes longer to effect than is generally believed, when dissolving the salt in water containing some thousandths parts of sesqui-carbonate of ammonium, and which, in my opinion, it is impossible to do in glass vessels.

To precipitate it, I slowly poured the solution of nitrate of calcium, when cold, into a saturated solution of oxalate of ammonium, having in suspension enough of this salt to convert all the nitrate of calcium used into oxalate. I did this so as not to have a greater volume of filtrate than I wished to examine with the first two washings, to see whether they contained any foreign solids.

After being undisturbed for twelve hours, the filtrate was decanted and passed through a purified filter-paper in a platinum funnel, and the oxalate of calcium was put into twice its own volume of water.

The filtrates were evaporated to dryness in a platinum dish, together with the first two washings.

The product of evaporation of the filtrates and washings, consisting of nitrate and oxalate of ammonium, was heated so as to drive off all volatile bodies. There remained a residue of oxide of calcium, weighing 0.041 grm., very strongly coloured yellow by platinate of calcium, and showing a very decided sodium spectrum, without a trace of a potassium or lithium spectrum.

The oxalate of calcium was washed by decantation. It was washed twenty times, using each time twice its volume of water; after being washed, the salt was dried on a water-bath, and converted into carbonate by raising it to a dull-red heat in the platinum dish which held it. I shall refer further on to this carbonate, which was quite white.

When introduced immediately after its preparation on a recently heated platinum dish, with an oxyhydrogen blowpipe, it coloured it yellow; this colour almost instantaneously changed to orange-red, and became deep red at the fusing-point of platinum. After the sodium was completely eliminated by exposing a new surface, the oxide of calcium spectrum shown was identical with that of oxide from the carbonate made from chloride and nitrate of calcium.

The last third, C, of the solution of nitrate of calcium from the spar, was converted into sulphate by pouring it into a quantity of absolute alcohol, acidulated with pure sulphuric acid. After the sulphate of calcium was deposited, I decanted the alcoholic filtrate, and turned the

precipitate into twice its own volume of alcohol at 60°, pouring it all into a platinum funnel provided with a clean linen plug, connected with a water-pump, passing weak alcohol through it so long as the washings turned blue litmus-paper red.

Directly after it was washed, the precipitated sulphate of calcium did not colour yellow either a Bunsen or a hydrogen flame, and showed no trace of the sodium spectrum. Of all the calcium compounds, the sulphate was the only one which showed this characteristic on being put into a flame. This fact was more surprising, because there is a double sulphate of calcium and sodium.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 16th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. A. J. Chapman, H. W. Dickinson, G. Goldfinch, E. Grossman, and A. F. Theodosius were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Henry Bentley, B.Sc., 116, Yarbrough Street, Moss Side, Manchester; Joseph John Bowley, 34, Elm Park Road, Chelsea; Daniel Bray, Broadmoor, Cinderford; Hugh Charles Herbert Candy, B.A., B.Sc., 101, Gower Street, W.C.; Thomas Ewan, B.Sc., Ph.D., Yorkshire College, Leeds; Charles James Pemeller Fuller, Mona House, Horwich, Lancs.; William Harrington, 11, Edgehill, Whitehaven; Albert Howard, 17, Elthiron Road, Fulham, S.W.; Ernest Haynes Jeffers, 50, St. John's Hill Grove, New Wandsworth, S.W.; James Johnstone, Braehead, Parkhill, Rutherglen; Charles Edward Sage, 7, Osney Crescent, N.W.

Of the following papers those marked * were read:—

*1. "The Acetylene Theory of Luminosity." By VIVIAN B. LEWES.

The author points out that in 1882 Professors Dewar and Living (Proc. Roy. Soc., xxxiv., 438) came to the conclusion that the "formation of acetylene in ordinary combustion seems to be the agent through which a very high local temperature is produced," whilst Guequen (Trans. Société Technique, 1884) claims to have put forward the acetylene theory of luminosity in 1884.

The author considers that the criticism offered against the acetylene theory by Smithells (Trans., 1895, lxvii., 1049) in no way affects the considerations upon which the theory is based, which are—

1. That the unsaturated hydrocarbons in the inner region of the flame are largely converted into acetylene before luminosity commences.
2. That acetylene develops luminosity when heated whilst flowing through a hard glass tube, no air being present.
3. That the temperature necessary to decompose acetylene with evolution of light does not raise to incandescence the carbon liberated by the decomposition.
4. That in luminous hydrocarbon flames of sufficiently high temperature the luminosity varies directly with the amount of acetylene present at the point where luminosity commences.

The objections raised by Smithells against the determination of absolute temperatures in flames by means of the Le Chatelier thermo-couple are warmly endorsed by the author as far as those portions are concerned in which combustion is taking place, and these objections were pointed out in his former paper (Proc. Roy. Soc., lvii., 452), but he contends that the results obtained in the

inner non-luminous portion of a hydrocarbon flame are probably fairly accurate, and the results obtained by Smithells fully confirm the statement that the temperature in the inner zone rises from a comparatively low temperature close to the burner to over 1000° at the apex of the zone.

The author describes experiments showing that although the heat of combustion of acetylene is very high, so small a proportion has to be burnt in order to develop the remaining energy as light and radiant heat that it by no means follows that the acetylene flame is hotter, or even as hot, as a coal-gas or ethylene flame of the same size.

Smithells has come to the conclusion that the statement that cyanogen could be made to undergo luminous combustion has arisen from a yellow ammonia flame having been mistaken for one containing solid carbon; the author shows that by surrounding the cyanogen flame by nitric oxide, intense luminosity and a copious deposit of soot can be obtained.

The author contends that the flame is in reality divided into two zones—

1. The outer sheath of combustion,
2. The inner region of non-combustion,

and that the latter consists of an internal portion in which radiant heat is converting the hydrocarbons into acetylene; a luminous envelope which caps it, and in which more intense heat is decomposing the acetylene with emission of light, and the blue calyx at the bottom of the inner zone where the hydrocarbons are undergoing decomposition by water vapour and carbon dioxide without previous separation of carbon.

The author also contends that the incandescent carbon particles in the upper portion of the flame are acted upon by carbon dioxide and water vapour forming carbon monoxide and hydrogen, and that this action tends far more than combustion by the air to prevent their escape from the flame.

DISCUSSION.

Professor SMITHELLS said that he had always considered the acetylene theory ingenious, and feared indeed that its very attractiveness had led Professor Lewes to a one-sided and, in many cases, an erroneous interpretation of evidence. The question was not whether the explanation of luminosity afforded by the acetylene theory was conceivable, but whether the theory was really in harmony with ascertained facts; and this question, he still thought, was to be answered decidedly in the negative. As Professor Lewes had not read the whole paper, but had only drawn the attention of the meeting to certain points, he was unable to say to what extent Professor Lewes had dealt with the series of objections raised to the theory, and his remarks must not, therefore, be regarded as pretending to be a complete reply.

He wished that Professor Lewes would state explicitly what view he had as to the structure of an ordinary gas flame. Did he, or did he not, accept the old and generally accepted view, that the flame consisted of three distinct parts—a luminous region, a mantle, and a blue calyx at the base? Professor Lewes had attempted to define the parts of flame by reference to temperatures; and whereas at one time he indicated the mantle as the region of lowest temperature, he now appeared to agree that it was the hottest part. Did he still maintain temperature measurements to be a reasonable basis for defining the anatomy of the flame?

He did not consider that Professor Lewes had explained the extraordinary discrepancies that had been pointed out in his measurements of temperature; and he should like to know whether Professor Lewes had used the thermo-couple, as shown in the apparatus before them, or whether he had not, as implied in his previous papers, inserted the twist of the thermo-couple in a manner now admitted to be improper.

He still thought that it was misleading to speak of 80 per cent of the unsaturated hydrocarbons as being con-

verted into acetylene within the flame. If acetylene were the source of light, and if the light depended on the almost explosive character of its decomposition, there surely was some reason to ask for evidence that a mixture of gases containing 1·4 per cent of acetylene, 0·5 per cent of other unsaturated hydrocarbons, and 98 per cent of other gases (four-fifths of which were incombustible) could afford light in the manner stated. He considered that such a doctrine was incredible.

The evidence now adduced by Professor Lewes to show not that the acetylene flame was comparatively cool, but that, conceivably it might be so if the fact were not otherwise, was very remarkable. He could not exactly say what was the mechanical equivalent of light, but his recollection was that it was extremely small, and he advised Professor Lewes to look into what was known on this subject before committing himself to the view that the acetylene flame lost so large a fraction of its total energy in the form of light. However, this seemed to be a matter of little consequence, for there was no getting over the fact that the acetylene flame was surrounded by a mantle of extremely high temperature, and that a platinum wire introduced into it glowed at least as brightly as the carbon within the flame. That being the case, there was no occasion to explain that, hypothetically, the flame might be cool.

With regard to the cyanogen flame, he had nothing to withdraw from what he had said on a previous occasion, though he congratulated Professor Lewes on having now made a new and interesting observation. He had entirely failed to obtain evidence of carbon being separated in a cyanogen flame surrounded by burning hydrogen, and Professor Lewes had not shown that it was separated. The use of nitric oxide (which would in its luminous result remind them of the behaviour of that gas towards carbon disulphide) undoubtedly led to the separation of carbon, and supplied a piece of evidence which Professor Lewes was now entitled to claim.

Much circumstantial evidence, believed by Professor Lewes to favour the acetylene theory, had been adduced. Among it was a calculation which, having a striking practical aspect, might have considerable influence on some minds, and he desired to ask Professor Lewes to explain and justify it. It was intended to give the theoretical illuminating value of ethane, ethylene, and acetylene respectively, on the supposition that, in giving light after passing through the state of acetylene, they were resolved into carbon and hydrogen, and this calculation gave results in tolerable agreement with the illuminating value of the gases as determined by the photometer. The calculation was, he thought, unintelligible from a scientific point of view, but, even if the principle were admitted, seemed not only incorrectly made, but capable of affording a set of numbers entirely at variance with practical measurements, just as easily as numbers in harmony with them. He thought some explanation of this was due from Professor Lewes. He would only, in conclusion, say again, that his remarks must not be taken at all as his complete answer to Professor Lewes, whose manner of presenting his paper had rendered this impossible.

Professor RÜCKER thought that the use of a thermocouple in a flame above the melting-point of one of the metals was open to grave objection, on account of the uncertainty as to the temperature which the junction actually attained. The validity of Professor Lewes's experiment on the thermal value of the luminous radiation depended on whether the whole of the non-luminous radiation had been absorbed in the comparison experiment. This in turn depended in part on the dimensions of the apparatus. By the solution of a small quantity of an iron salt the absorptive power of the water would have been increased, while the light would not have been very largely diminished.

Professor THORPE remarked that a possible fallacy might underlie the deductions as to temperature drawn from the behaviour of a platinum wire in a flame con-

taining free carbon and carbonic oxide, on account of the specific chemical action which those substances might exert on the metal. The fact that a platinum wire would melt even in an ordinary candle-flame, which is not particularly hot, was known to Smithson Tennant, and is referred to by Davy, in his well-known paper. Davy also found that a filament of platinum could be fused by a flame of cyanogen in air, whereas the same wire was not melted by a hydrogen flame.

Mr. GROVES drew attention to Professor Lewes's statement, that the yellow light emitted by a jet of cyanogen when surrounded by a hydrogen flame was due to carbon liberated by the decomposition of the cyanogen, and suggested that if the image of the sun were thrown on to this flame by means of a lens, and the reflected light examined by methods familiar to physicists, it would be easy to ascertain whether the flame contained solid particles. In that case, not only would the light be found to be polarised, but, if examined spectroscopically, would exhibit the Fraunhofer lines. If the flame contained no solid particles, then the luminosity could not be due to liberated carbon; on the other hand, even if it were found to contain solid particles, it would not necessarily follow that these were carbon.

The PRESIDENT referred to a suggestion of Professor Lewes, that the great output of light from the acetylene flame may leave the flame itself comparatively cool. He thought that of the energy made kinetic by chemical changes within the flame, only a small part radiated out in waves of such a length as to be light. The small carbon particles in the flame lost much heat by radiation, and would thus be cooler than the non-radiating gases in which they floated. It was agreed that the outside of a flame was the hottest part. One of the causes of the splendour of the flame of pure acetylene was, no doubt, the high temperature to which the separation, as well as the oxidation, of the carbon and hydrogen contributed; but a suitable burner was necessary: the flame must have a large outer surface, and close within this must be spread, over the whole frontier, the little particles of carbon which glow for an instant and disappear.

Among the causes which make the flame of one gas brighter than that of another, might be a difference in the size and number of these solid particles. As one salt gave a large-grained and another a small-grained precipitate, so it might be with decomposing hydrocarbons; and as a given quantity of platinum wire coiled into a spiral, and held in a Bunsen flame, would give more light the smaller the gauge so the finer dust of carbon might make the brighter flame.

Some idea of the proportion between the surface of the flame and the actual surface of the glowing particles to which its light is due might be gained from a comparison with the filament of an electric glow-lamp. The radiating substance was similar in the two cases, and when the filament and current were such that the glow-lamp gave light of the same amount and colour as the gas-flame, it was likely that the glowing surfaces had a similar area.

Professor LEWES, in reply, said that he extremely regretted not having read his paper *in extenso*, as it contained answers to most of the objections advanced by Professor Smithells.

His views as to the structure of an ordinary gas-flame were that it contained four parts, but that three of these, namely, the non-luminous inner zone, the luminous sheath, and the blue calyx, were portions of the region in which no combustion, in the ordinary acceptance of the term, took place; whilst the outer mantle of the flame was the region of intense combustion, and is undoubtedly the hottest part of the flame. In a paper read in 1892, he had given a description of the structure of a gas-flame, but, in criticising this, Professor Smithells had evidently overlooked the fact that the portion of the paper following the description was devoted to an investigation as to the causes which led to the non-luminosity of hydro-

carbon flames, which showed that the outer envelope must be the hottest portion of the flame; but it is also manifest that the outer side of this mantle must be rapidly cooled by admixture with air and products of combustion, so that the maximum temperature will be near the inner side of this region, and it was the extreme outer portion of this zone which he had described in the words criticised by Professor Smithells.

He thoroughly agreed in condemning any temperature measurements of those portions of the flame in which active combustion was going on, but still believed in the measurements obtained in the area of non-combustion. Professor Smithells had pointed out that serious discrepancies existed between the temperatures recorded in a flat flame in the 1892 paper and in the 1895 paper, but as the one was from a No. 6 Bray, whilst the other was given by a 0000 Bray, it was difficult to understand on what grounds it could be expected that they would show any agreement, as the temperatures varied for every alteration in the size of the burner, and for every variation in the pressure at which the gas was burnt.

One of Professor Smithells' strongest points was that it was misleading to speak of 80 per cent of the unsaturated hydrocarbons being converted into acetylene within the flame—the statement he had made was that 80 per cent of the unsaturated hydrocarbons at the point just before luminosity commenced consisted of acetylene.

If a mixture of 1.5 per cent of acetylene and any gas which had a non-luminous flame was burnt, no luminosity would be generated, and no trace of acetylene would be detected at the top of the inner zone, it having been consumed before the temperature necessary for its decomposition was reached; but if 1.5 per cent of acetylene was led into the top of the inner zone of a flame of coal gas, from which the unsaturated hydrocarbons had been absorbed, then this addition would make the flame as luminous as if the unsaturated hydrocarbons had not been withdrawn, and he thought that Professor Smithells' doubt as to the truth of the acetylene theory was based largely on a misconception of this point.

As regards the experiments to show that a flame radiates a considerable amount of energy when emitting light, he was perfectly in accord with those who pointed out that the amount of energy converted into light was but small; there was also a large amount of heat radiated, and the experiment with the blackened bulb would give the total radiation cut off by the opaque coating, which when the flame was radiating freely would be lost to the flame. It would be preposterous to lay any great stress on this experiment, as the products of combustion were practically escaping uncooled.

He had made in a former paper a calculation to show that a ratio existed between the heat of formation of a hydrocarbon and its illuminating value, but he had been careful to point out that in our present absence of knowledge as to the heat relations existing at high temperatures, any such calculations were valueless except as showing that the greater the endothermic value of a compound the higher was its illuminating value.

Professor Smithells concludes that because a platinum wire held in the outer shield of a flame glows with the same incandescence as the carbon particles in the flame itself, therefore there is no need to assume any other source of heat than that given by the combustion going on in the flame walls.

He thought that this conclusion was based upon at least two fallacies. In the first place Professor Smithells had himself clearly pointed out that there is a temperature gradient on the horizontal plane in which there is an abrupt rise in temperature from the luminous sheath to the point of maximum combustion in the external envelope, and it therefore follows that the platinum wire held in the external envelope must be heated to a higher temperature than the carbon particles in the luminous sheath. Secondly, the conclusion is based upon the assumption that the emissive power for light of carbon and platinum

is the same, which is highly improbable. It has been shown that metals at high temperatures reflect light, and he thought it quite possible that some of the apparent brightness of the platinum wire might be due to light reflected from the luminous veil in front of which the wire was placed.

(To be continued).

NOTICES OF BOOKS.

Spectrum Analysis. ("Die Spectral Analyse"). By Dr. JOHN LANDAUER. Brunswick: Vieweg and Son. 1896. 8vo., pp. 174.

WE have here a most useful guide to spectroscopic analysis as applied in chemistry, physics, and astronomy. The author expresses his regret that this branch of scientific investigation, though it met with its origin in Germany, has not there met with the attention and general application which it so fully merits.

A history of spectroscopy is carried down from the first recognition of the yellow sodium flame by Thomas Melville, in 1752. His observations were followed up successively by John Herschel, Fox Talbot, W. A. Miller, and Swan, but the formal development of spectroscopy was reserved for Kirchhoff and Bunsen in 1859; their epoch-making memoir, "Chemical Analysis by Spectral Observations" ("Chemische Analyse durch Spectral Beobachtungen"), appeared in *Poggendorff's Annalen*, cx., 167. We next pass to the physical foundations of the methods, including the principles of the gratings as developed by Rutherford, and especially by Rowland. The spectroscopes of Kirchhoff and Bunsen, of Steinheil, of Browning, of Rutherford, and Thallon are figured and described. The direct-view spectroscopes of Amici, Janssen, and Browning and Christie are also represented; as also Sorby's micro-spectroscope. A modification of this last instrument is designed by Abbe and executed by Carl Zeiss, of Jena.

Particular notice is given—as it is fully due—to the spectrograph, a combination of the spectroscope with a photographic camera. Not the least important feature of solar and stellar spectroscopy is that it furnishes a convenient refutation of the erroneous dogma that the more general sciences, whilst they give aids to the more special disciplines, receive nothing in return.

As spectral auxiliaries, Dr. Landauer describes the appliances for obtaining flame spectra, spark spectra, the phenomena due to the silent discharge in Geissler tubes, as also the observation of the ultra-violet and ultra-red. There is a brief mention of Becquerel's phosphoscope. We find no notice of the improved phosphoscope of Crookes, and of its use in chemical research.

We come next to absorption-spectra, the source of light which they require, and the most convenient vessels for containing the solutions to be examined. For this purpose H. W. Vogel uses ordinary test-tubes. The arrangements for measurement and the scale are various; Bunsen places the yellow soda-line at 50, whilst Vogel fixes it at 0°.

The author distinguishes three kinds of spectra—the continuous, the fluted or grooved spectrum, and the line spectra. The influence of temperature and pressure are carefully considered. The cause of the origin of the Fraunhofer line is definitely shown. The influence of the state of aggregation, of the temperature of the solvent, &c., are next explained. Of the relations between the spectra of the different elements proposed by Lecoq de Boisbaudran, Ditte, Troost and Hautefeuille, Ciamician, Hartley, Grünwald, and Ames, those of the first and last mentioned authorities only seem to have maintained their position.

In the special part of the work we find the spectral characteristics of each element very fully laid down, as

far as the emission spectra are concerned. A similar treatment of the absorption spectra presents great difficulties, and has not yet been carried out.

Abney and Festing have not succeeded in detecting chlorine, bromine, and iodine in organic combinations.

In what may be called the astronomical portion of the work, we find, firstly, an account of the solar spectrum, as laid down in Rowland's table of wave-lengths. Many of the most important of the Fraunhofer lines are still not explained. The spectra of fixed stars of the third (least brilliant) class is conjectured to indicate the presence of a carbon compound (acetylene?).

In many respects this work is admirably calculated for the convenience of the student. Besides the table of contents, there is a double index, of the authors quoted and of the subjects. The biographical notes are very copious. A few only of the most recent books and memoirs have remained unnoticed.

To *savants* engaged with spectral research—would they were more numerous!—this book must be most strongly recommended.

CORRESPONDENCE.

ESTIMATION OF INSOLUBLE PHOSPHATE.

To the Editor of the Chemical News.

SIR,—With regard to the above and Mr. Allibon's letter (CHEMICAL NEWS, vol. lxxiii., p. 47), I can only say that with care very good results can be obtained with the modification I suggested of the uranium method.

I am quite aware of the disturbance caused by any considerable amount of iron and alumina, and if the manure contains much of these substances the process will not work; but in ordinary cases the quantity is very small, and works' chemists who analyse the materials will have some knowledge on this point.

I do not for a moment propose that the uranium method should supplant the usual gravimetric one; but there are times when works' managers require information without delay, and in such cases my proposal seems the only one available.

I may say my attention was first called to this matter by seeing the method mentioned in a text-book in use at the College of Science in Ireland.

As to the amount taken for analysis, 0.5 grm. is certainly small; but if the amount is large, and the "soluble" is also estimated by uranium, a low result will almost certainly be found, which is a more serious matter. A friend, whose ability and accuracy are beyond question, went into the whole matter in my laboratory, and clearly proved that if accurate results are desired it is unsafe to take more than about 0.5 grm. for the determination.

The uranium method still fills so much space in valuable text-books that I think I need make no apology for drawing further attention to it.—I am, &c.,

VINCENT EDWARDS,
Chemist to Messrs. Lawes & Co., Lim.

West End Pathological Laboratory,
55, Weymouth Street, Portland Place, W.

ON THE PRESENCE OF GOLD IN SILVER ORES.

To the Editor of the Chemical News.

SIR,—That small quantities of gold are to be found in many silver ores has been known for a long time; yet it constantly happens that the analytical chemist is only asked to determine the number of ounces of silver per ton of ore. Of course, the determination of the gold also makes the assay rather more expensive, but this slight economy is apt to prove "penny wise, pound foolish." It

is quite possible that the gold in some silver ores may have been overlooked for a long time. Here is a specimen of my own experience on this subject.

Many years ago I received from the late Sir James Anderson, of the Eastern Telegraph Co., a large batch of silver ore from the celebrated Comstock lode in California. The silver was present in various forms, but chiefly as sulphide, and as grey copper ore. I was requested simply to determine the amount of silver present, but I specially mentioned on the analysis sheet that the ore contained very appreciable quantities of gold also. To this intimation no attention appears to have been given. Many months afterwards, I took up one of the small fragments of rock not included in the powdered samples sent for assay. It was a compact feldspathic rock of a light reddish brown colour, with thin streaks of what appeared to be sulphide of silver running through it, something like certain specimens of selenide of lead which I met with in the Hartz district. As it was evidently a rich specimen, I made an assay of it from pure curiosity, and, to my surprise, the button came out yellow instead of white; it contained much more gold than silver. A second assay, made with another fragment, also gave a yellow button, but lighter in colour and containing more silver. It would appear probable, therefore, that tellurium gold (sylvanite) accompanies the sulphide of silver (fahlerz, stephanite, &c.) in this rich Comstock lode, and has evidently been overlooked.

I may mention on this occasion that in olden times Vauquelin reported 1 to 10 per cent of platinum in some samples of fahlerz (grey copper ore), and F. Field found over 1 ounce of gold and 26½ ounces of silver in another sample of grey copper ore. If that quantity of gold could be extracted, it alone would more than pay the raising of the ton of ore, not to mention the copper and silver present. It is very probable that some of the Cornish grey copper ore may be found to yield gold also.—I am, &c.,

T. L. PHIPSON.

The Casa Mia Laboratory, Putney,
London, S.W., Feb. 7, 1896.

PREPARATION OF PURE ANHYDROUS HYDROCYANIC ACID.

To the Editor of the Chemical News.

SIR,—The following are original, easy, and direct methods of preparing pure anhydrous hydrocyanic acid:—

1. By the reaction of sulphuric acid, slightly diluted (to the strength of the ordinary brown oil of vitriol), or concentrated hydrochloric acid, on cyanide of sodium. In the first instance the reaction is so violent that the greater portion of the hydrocyanic acid passes over without the application of heat; but afterwards just sufficient will have to be applied to drive over the remainder of the acid.

2. By distilling cyanide of calcium with concentrated sulphuric or hydrochloric acid. As in the first process, the greater portion of the prussic acid passes over without heat being applied.

3. By passing dry arseniuretted hydrogen gas over perfectly dry potassium cyanide, gently heated in a glass tube connected with a small receiver cooled by a freezing mixture.

4. By distilling cyanide of lead with glacial acetic acid. There is another simple method which I have not yet tried, though it would doubtless succeed, viz., by distilling powdered Prussian blue (prussiate or ferrocyanide of iron) in hydrochloric acid gas.

I find that cyanide of arsenic, $As(CN)_3$, which I discovered several years ago, is best obtained by the reaction of arsenious chloride on sodium or calcium cyanide; also by distilling cyanide of lead with arsenious chloride—or sulphide, perhaps.—I am, &c.,

G. W. BLYTHE.

Manor Cottage, Dodinghurst,
near Brentwood, Essex, February 1, 1896.

CHEMICAL NOTICES FROM FOREIGN
SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., No. 3, January 20, 1896.

Circulation of Air in the Soil.—P. P. Dehérain and M. Demoussy.—The experiments of the authors show the great advantage of liming strongly argillaceous soils. The lime, by hindering their clay from passing into suspension, preserves their porous structure, their reserves of moisture, and ensures the free circulation of the air. The action of lime is very different in different soils. If incorporated with a clay soil capable of breaking up under the action of prolonged rain, lime is useful, since it prevents the production of impermeability; but if, on the contrary, the soil resists water without breaking up, the addition of lime has in this respect no reason. We may thus tell the cultivators of strong soils that if, after heavy rains, they see water standing in their furrows, they should add lime or marl in order to secure the free circulation of air and moisture.

A Crookes's Tube of a Spherical Form showing the Reflection of the Kathode Rays by the Glass and the Metal.—Gaston Séguin.—A hollow sphere of glass in which a vacuum has been made to one-millionth of an atmosphere contains an electrode of aluminium in the shape of a star, placed at its centre. A second electrode has the form of a small disc, applied against the glass wall parallel to the star. If we introduce the apparatus in the circuit of an induction coil which yields sparks of 10 c.m., the disc being at the negative pole, we observe luminous phenomena which demonstrate the reflection of the kathode rays from the glass and the metal. The sheaf of kathode rays emitted strikes and illuminates the opposite wall; we see the black shadow of the star in the midst of the luminous spot. These same rays, being reflected on the glass, return to illuminate the glass wall, and form a second shadow of the star, larger than the first. Lastly, the aluminium star reflects a part of the sheaf. Hence there results a luminous projection of this star in the middle of the shadow of the same star formed on the wall. If we take the aluminium star as kathode, the luminous phenomena are simplified. We merely see the star projected on the glass walls opposite, giving two luminous images in their true size.

Solubility of Sodium Thiosulphate in Alcohol.—P. Parmentier.—The solubility of the three modifications of thiosulphate (hyposulphite), the ordinary, the modified, and the superfused, increases with the temperature and with the degree of dilution.

Iron Nitrososulphides.—C. Marie and R. Marquis.—The authors give to these compounds, called by their discoverer, Roussin, nitrosulphides, the name nitrososulphides. The crystals obtained are black; they are soluble in water, alcohol, and especially in ether, in chloroform, acetone, and acetic ether, but insoluble in benzene and ligroine. Their percentage composition is:—Iron, 38.64; sulphur, 15.50; nitrogen, 16.36; water, 6.62; oxygen (by difference), 22.88. These figures lead to the crude formula $\text{Fe}_3\text{S}_2\text{N}_5\text{O}_6 + \text{H}_2\text{O} \cdot 5$.

NOTES AND QUERIES.

** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Chemically Pure CS_2 .—Having occasion to use some chemically pure, odourless CS_2 , I should be much obliged if any of your readers could give me the name of any firm from whom I could get some.—J. K. W.

MEETINGS FOR THE WEEK.

- MONDAY, Feb. 10th.—Society of Arts, 8. (Cantor Lectures). "Alternate Current Transformers," by Dr. J. A. Fleming, F.R.S.
Medical, 8.30.
- TUESDAY, 11th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.
Institute of Civil Engineers, 8.
Medical and Chirurgical, 8.30.
Photographic, 8. (Anniversary).
- WEDNESDAY, 12th.—Society of Arts, 8. "Water Purification by means of Iron," by Sir Douglas Galton, F.R.S.
Pharmaceutical, 8.30.
Sanitary Institute, 8. "Influence of Subsoil Water on Health," by S. Monckton Copeman, M.D.
- THURSDAY, 13th.—Royal, 4.30.
Royal Institution, 3. "Some Aspects of Modern Botany," by Prof. H. Marshall Ward, F.R.S.
Institute of Electrical Engineers, 8.
Mathematical, 8.
- FRIDAY, 14th.—Royal Institution, 9. "Fish Culture," by J. J. Armistead.
Astronomical, 3. (Anniversary).
Physical, 5. (Annual Meeting). "Determination of High Temperatures with the Meldometer," by W. Ramsay and N. Eumorfopoulos.
- SATURDAY, 15th.—Royal Institution, 3. "Realism and Idealism in Musical Art," by Prof. C. Hubert H. Parry, D.C.L., &c.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1890.

ON THE X RAYS.

PROF. RÖNTGEN'S great discovery leads, as it might have been expected, to no little discussion. No one, indeed, denies the existence of the phenomena observed, but on their origin and their nature there is as yet little accord. Prof. Slaby, of Charlottenburg, has failed in obtaining the rays with a Crookes's vacuum tube, but has succeeded in producing them with what we may call a home-made tube, in which the vacuum was equal to 0.002 m.m. of mercury. He has also obtained good photographs with "Lenard rays,"—i. e., kathode rays which have travelled outside the tube in which they had been produced.

Prof. Röntgen does not accept the hypotheses which identify the X rays with either the ultra-red, the visible, the ultra-violet rays (such as have been hitherto studied), or the Lenard rays, and he gives important marks of difference.

Perhaps the best way to ascertain the nature of the X rays will be to work with them.

A correspondent, whose name we are not at liberty at present to make known, raises the question whether Prof. Röntgen's X rays permeate distilled water in a different manner from water containing invisible impurities, or, in a word, can they serve as an auxiliary agent in the hygienic analysis of waters?

He also suggests the use of a vacuum tube consisting not of glass, but of aluminium.

PHOTOGRAPHY WITH DARK LIGHT.

By GUSTAVE LE BON.

THE recent publication of experiments in photography, with light of a cathodic origin, has induced me to make known—though they are as yet very incomplete—some of the experiments which I have been conducting for two years on photography, through bodies which are opaque to ordinary light. The two subjects are very different, though the results present some analogies.

The following experiments prove that ordinary light, or at least some of its radiations, traverses without difficulty the most opaque bodies. Opacity is a phenomenon existing merely for an eye like ours; if constructed a little differently it could easily see through walls.

In an ordinary positive photographic case we introduce a sensitive plate, and above it any photographic proof whatever; then we place above the proof, and in close contact with it, a plate of iron covering entirely the front of the case. We expose the plate, thus masked by the iron plate, to the light of a petroleum lamp for about three hours. An energetic and prolonged development of the sensitive plate pushed to a total blackening will give, by transference, an image of the proof, very pale but very distinct.

If we slightly modify the above experiment, we obtain images almost as strong as if no obstacle had been interposed between the light and the sensitive plate. Without any change in the above arrangement, let us place behind the sensitive plate a sheet of lead, of any thickness, and bend down its edges so as to cover slightly the sides of the iron plate. The sensitive plate and the proof are thus imprisoned in a sort of metal case, the front of which is formed of the plate of iron, whilst the back and the sides are formed by the plate of lead. After an ex-

posure of three hours to the petroleum lamp, we obtain on development a strong image.

What is the part played by the sheet of lead in the second experiment? Provisionally, I suppose that the contact of the two metals gives rise to very feeble thermoelectric currents, the action of which is added to that of the luminous radiations which have traversed the iron plate.

I hope in future to succeed in ascertaining the rôle of the various factors which may come into play in producing the above results. I hope to be able to determine the properties of light after its passage through opaque bodies. The action which might be exerted by heat or by light stored up on the proofs has been already entirely eliminated in my experiments.

Sunlight gives the same results as the light of petroleum, and does not seem to act much more energetically.

Cardboard and metals—especially iron and copper—are easily traversed by light. The passage of light through the most opaque bodies is merely a question of time.

If we repeat the above experiments in the photographic camera,—i. e., if we place a metal plate before the sensitive plate, and consequently between this latter and the object to be photographed,—we obtain in two hours, with the sun, on developing, an intense blackening of the sensitive plate, which proves the passage of the light through the opaque screen; but we obtain images only very exceptionally, and under conditions which I have not yet been able to determine.

I have given to these radiations of an unknown nature, which thus pass through opaque bodies, the name of *dark light*, on account of its invisibility to the eye. On considering the difference between the number of vibrations which produce the different forms of energy, such as electricity and light, we may suppose that there exist intermediate members corresponding to natural forces still unknown. These latter may be connected by insensible gradations with the forces which we know. The possible forms of energy may be infinite in number. *Dark light* perhaps represents one of these forces which we do not know.—*Comptes Rendus*, cxvii., p. 188.

Before making known the new results of my researches on dark light, I give some indications destined to facilitate the reproduction of these experiments.

As the rapidity of the action of commercial photographic plates varies in the proportion of 1:4, it is evident that if, in order to obtain an image, we require three hours of exposure with very rapid plates, then on making use of plates of a rapidity of four times less we should obtain no result. Nor do we obtain a result if we do not make use of a developing agent sufficiently energetic.

I have taken care to explain (see above) that I have eliminated two factors of error; the possible influence of heat and that of light stored up in the proofs. After having used several methods, one of the most simple being to cut the proof in two parts and employ these parts for comparative experiments, I finally adopted a procedure consisting in using only proofs which had remained for a day in darkness in contact with a sensitive plate without giving any veil on developing. If such proofs then give images after exposure behind metallic plates, such images can evidently be due only to the influence of the dark light. I use always, moreover, the same proofs. As they are not taken out of their cases except in the laboratory, they cannot receive any other light than that which has passed through the metal plates; that is to say, dark light.

As for heat, I have satisfied myself, by keeping sensitive plates in contact with the proofs at a dark heat of 50°, that we do not obtain any trace of an image.

I have only made use of petroleum lamps for the sake of having a constant light. Daylight gives better results, but its intensity is too variable to allow of comparative experiments.

It is by no means necessary for the opaque plates to be in contact with the proofs. We obtain the same results if we place the plates at a small distance, so as to isolate the sensitive plate and the proof from all metallic contact.

I have the honour of submitting to the Academy negatives obtained as I have just described, through metal plates of about 0.5 m.m. in thickness.

The first negative has been obtained through a plate of aluminium, a metal very transparent for the dark rays. The image is as strong as if it had been obtained by the ordinary procedures.

The second image has been obtained with a thick medal of aluminium, simply laid on the case with its sides protected with black paper. The transparency of aluminium for dark light is such that we obtain an image of the upper surface of the medal by an exposure of less than two hours. I must add that the medal did not press upon the sensitive plate, as it was separated from this latter by the glass plate of the case.

The third image has been obtained through a plate of brass $\frac{1}{10}$ m.m. in thickness. This metal is likewise very permeable to the dark rays. The image is very distinct, but incomplete, since it occupies only the central part of the negative.

The fourth image has been obtained through a plate of sheet iron. It is very pale, but quite distinct.

On account of certain technical difficulties, I have not completed the exact determination of the degree of relative permeability of opaque bodies for the dark rays. I can, however, indicate that aluminium and copper are the most transmissive. Iron is less permeable. Zinc, silver, and tin are very slightly permeable. Black paper, and especially pasteboard covered with black paper, are transmissive to an infinitely slight extent.

Black paper, the kind employed for wrapping up packages of photographic plates, is one of the substances least readily permeable by the dark rays, notwithstanding its slight thickness ($\frac{1}{10}$ of 1 m.m.). If we superimpose black paper upon cardboard (which is exactly the process for packing up photographic plates) the opacity for the dark rays is almost complete, of course for brief exposures.

It will be remarked that the rays of cathodic origin pass very easily through the dark paper, though the dark rays scarcely traverse them. This is not the only distinction between the dark rays and those of cathodic origin.

I am about to examine within what limits the dark rays obey the laws of refraction and the deviations which they undergo in a magnetic field. Some of the results obtained caused me to believe that the dark light is composed of radiations of a different nature.—*Comptes Rendus*, cxii., p. 233.

OBSERVATIONS ON G. LE BON'S RECENT NOTES ON DARK LIGHT.

By G. H. NIEVEGLOWSKI.

I HAVE repeated Le Bon's experiment in darkness *without any source of light*. The result has been the same as that of Le Bon, which seems to indicate that the image developed on the sensitive plate is derived from the luminous energy stored up by the proof when taking positive proofs, energy which it has preserved and communicated to the sensitive plate.

With this fact we may associate the following, indicated for the first time by Laoureux, and which I have frequently had the opportunity to observe:—

A plate exposed in the camera and not developed, being fixed in contact with, or at a small distance from, another sensitive plate which has not undergone the action of light, we may detect an image on *both*, the second being the feebler. These experiments, which do

not succeed with all plates, seem, as Eder has said with reference to those of Laoureux, to be due to a kind of phosphorescence of the gelatin.—*Comptes Rendus*, cxii., p. 232.

NEW PROPERTIES OF THE X RAYS.

By L. BENOIST and D. HURMUZESOU.

IN view of the various hypotheses by which an explanation of the recent experiments on the X rays has been attempted, we have endeavoured to study the action of these rays outside of, and rather far from, the Crookes tube in which they are produced,—action upon electrified bodies withdrawn at once from every luminous action, and from all external electric action.

We have caused the rays of a Crookes tube, incited by a powerful coil, to act upon the gold leaves of an Hurmuzesou electroscope at the distance of about 20 c.m. from the tube, and alternately charged with positive and negative electricity.

In this electroscope the insulated conductive system is in the interior of a Faraday cylinder formed of a rectangular metal cage put in communication with the earth, and which is closed by two movable windows, the nature of which can be charged at will. The insulation obtained by a disc of dielectricine which closes the tube admits of a perfect preservation of the charge for several months.

By successively substituting the window opposite to the Crookes tube for the plates specified below, we obtain the following results:—

The X rays immediately and completely discharge the electroscope, more rapidly if the charge is negative than if it is positive. This action is produced across plates of metal (aluminium), forming a perfect screen, as well from a luminous as from an electrical point of view. It is produced with very different degrees of rapidity, according to the nature and thickness of the bodies interposed. We have thus a new way of investigation applicable to the study of these rays, and enabling us to gain important indications as to their real nature.

This is the summary of our present experiments:—

The plate to be studied being put in its place, the electroscope charged to about a divergence of 40°, the keeping-tube replaced, and the Crookes tube set in activity, we have observed:—

1. Black paper (sixteen leaves interposed), the collapse of the gold leaves is immediate and complete in a few seconds; they do not rise again.
2. Plate of brass ($\frac{1}{10}$ m.m. in thickness), no change in the divergence of the gold leaves.
3. Plate of aluminium ($\frac{1}{10}$ m.m.), immediate fall, complete in a few seconds; same result with plates of aluminium up to 1 m.m. and even upwards, and the Crookes tube being removed to the distance of 30 c.m.; the complete collapse of the gold leaves scarcely requires a few seconds more.

We have carefully verified the electric value of the metal screen formed by the cage and the plate connected with the earth.

The substances easily traversed are silver in beaten leaves, leaves of paper steeped in metallic solutions, vulcanised fibre, gelatin, celluloid, ebonite, &c.

The substances not traversed, at least in the thicknesses employed, are brass, zinc, glass, and unglazed porcelain (3 m.m.).

We purpose developing the use of a method for the investigation of the X rays.—*Comptes Rendus*, cxii., p. 235.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne presiding. The following were elected Members:—Mrs. Montagu, Mr. Robert R. Tatlock, F.C.S., and Mr. Ernest Westlake.

ON SOME PHYSICAL PROPERTIES OF ARGON AND HELIUM.*

By Lord RAYLEIGH, Sec. R.S.

Density of Argon.

IN our original paper (Rayleigh and Ramsay, *Phil. Trans.*, clxxxvi., A, pp. 221, 238, 1895) are described determinations by Prof. Ramsay, of the density of argon prepared with the aid of magnesium. The volume actually weighed was 163 c.c., and the adopted mean result was 19.941, referred to $O_2=16$. At that time a satisfactory conclusion as to the density of argon prepared by the oxygen method of Cavendish had not been reached, although a preliminary result (19.7) obtained from a mixture of argon and oxygen (*loc. cit.*, p. 221) went far to show that the densities of the gases prepared by the two methods were the same. In order further to test the identity of the gases, it was thought desirable to pursue the question of density; and I determined, as the event proved, somewhat rashly, to attempt large scale weighings of pure argon with the globe of 1800 c.c. capacity employed in former weighings of gases (*Roy. Soc. Proc.*, Feb., 1888; Feb., 1892; March, 1893) which could be obtained in quantity.

The accumulation of the 3 litres of argon, required for convenient working, involved the absorption of some 300 litres of nitrogen, or about 800 litres of the mixture with oxygen. This was effected at the Royal Institution with the apparatus already described (*Phil. Trans.*, l. c., p. 219), and which is capable of absorbing the mixture at the rate of about 7 litres per hour. The operations extended themselves over nearly three weeks, after which the residual gases amounting to about 10 litres, still containing oxygen with a considerable quantity of nitrogen, were removed to the country and transferred to a special apparatus where it could be prepared for weighing.

For this purpose the purifying vessel had to be arranged somewhat differently from that employed in the preliminary absorption of nitrogen. When the gas is withdrawn for weighing, the space left vacant must be filled up with liquid; and afterwards, when the gas is brought back for re-purification, the liquid must be removed. In order to effect this, the working vessel, Fig. 7 (*Phil. Trans.*, l. c., p. 218) communicates by means of a syphon with a 10-litre "aspirating bottle," the ends of the syphon being situated in both cases near the bottom of the liquid. In this way the alkaline solution may be made to pass backwards and forwards, in correspondence with the desired displacements of gas.

There is, however, one objection to this arrangement which requires to be met. If the reserve alkali in the aspirating bottle were allowed to come into contact with air, it would inevitably dissolve nitrogen, and this nitrogen would be partially liberated again in the working vessel, and so render impossible a complete elimination of that gas from the mixture of argon and oxygen. By means of two more aspirating bottles an atmosphere of oxygen was maintained in the first bottle, and the outermost bottle—connected with the second by a rubber hose—gave the necessary control over the pressure.

Five glass tubes in all were carried through the large rubber cork by which the neck of the working vessel was closed. Two of these convey the electrodes: one is the syphon for the supply of alkali, while the fourth and fifth are for the withdrawal and introduction of the gas, the former being bent up internally, so as to allow almost the whole of the gaseous contents to be removed. The fifth tube, by which the gas is returned, communicates with the fall-tube of the Töpler pump, provision being made for the overflow of mercury. In this way the gas, after weighing, could be returned to the working vessel at the same time that the globe was exhausted. It would be

tedious to describe in detail the minor arrangements. Advantage was frequently taken of the fact that oxygen could always be added with impunity, its presence in the working vessel being a necessity in any case.

When the nitrogen had been so far removed that it was thought desirable to execute a weighing, the gas on its way to the globe had to be freed from oxygen and moisture. The purifying tubes contained copper and copper oxide maintained at a red heat, caustic soda, and phosphoric anhydride. In all other respects the arrangements were as described in the memoir on the densities of the principal gases (*Roy. Soc. Proc.*, liii., p. 134, 1893), the weighing globe being filled at 0° , and at the pressure of the manometer gauge.

The process of purification with the means at my command proved to be extremely slow. The gas contained more nitrogen than had been expected, and the contraction went on from day to day until I almost despaired of reaching a conclusion. But at last the visible contraction ceased, and soon afterwards the yellow line of nitrogen disappeared from the spectrum of the jar discharge.* After a little more sparking, a satisfactory weighing was obtained on May 22, 1895; but, in attempting to repeat, a breakage occurred, by which a litre of air entered, and the whole process of purification had to be re-commenced. The object in view was to effect, if possible, a series of weighings with intermediate sparkings, so as to obtain evidence that the purification had really reached a limit. The second attempt was scarcely more successful, another accident occurring when two weighings only had been completed. Ultimately a series of four weighings were successfully executed, from which a satisfactory conclusion can be arrived at.

May 22	3.2710
June 4	3.2617
June 7	3.2727
June 13	3.2652
June 18	3.2750
June 25	3.2748
July 2	3.2741

The results here recorded are derived from the comparison of the weighings of the globe "full" with the mean of the preceding and following weighings "empty," and they are corrected for the errors of the weights and for the shrinkage of the globe when exhausted, as explained in former papers. In the last series, the experiment of June 13 gave a result already known to be too low. The gas was accordingly sparked for fourteen hours more. Between the weighings of June 18 and June 25 there were nine hours' sparking, and between those of June 25 and July 2 about eight hours' sparking. The mean of the last three, viz., 3.2746, is taken as the definitive result, and it is immediately comparable with 2.6276, the weight under similar circumstances of oxygen (*Roy. Soc. Proc.*, liii., p. 144, 1893). If we take $O_2=16$, we obtain for argon—

19.940,

in very close agreement with Professor Ramsay's result.

The conclusion from the spectroscopic evidence, that the gases isolated from the atmosphere by magnesium and by oxygen are essentially the same, is thus confirmed.

The Refractivity of Argon and Helium.

The refractivity of argon was next investigated, in the hope that it might throw some light upon the character of the gas. For this purpose absolute measurements were not required. It sufficed to compare the pressures necessary in two columns of air and argon of equal

* Jan. 29.—When the argon is nearly pure, the arc discharge (no jar connected) assumes a peculiar purplish colour, quite distinct from the greenish hue apparent while the oxidation of nitrogen is in progress, and from the sky-blue observed when the residue consists mainly of oxygen.

* A Paper read before the Royal Society, January 16th, 1896.

lengths, in order to balance the retardations undergone by light in traversing them.

The arrangement was a modification of one investigated by Fraunhofer, depending upon the interference of light transmitted through two parallel vertical slits placed in front of the object-glass of a telescope. If there be only one slit, and if the original source, either a distant point or a vertical line of light, be in focus, the field is of a certain width, due to "diffraction," and inversely as the width of the slit. If there be two equal parallel slits whose distance apart is a considerable multiple of the width of either, the field is traversed by bands of width inversely as the distance between the slits. If from any cause one of the portions of light be retarded relatively to the other, the bands are displaced in the usual manner,

in the horizontal direction only, for the spherical lenses of ordinary eyepieces. For many purposes a single lens suffices, but it must be of high power. In the measurements about to be described most of the magnifying was done by a lens of home manufacture. It consisted simply of a round rod, about $\frac{1}{2}$ in. (4 m.m.) in diameter, cut by Mr. Gordon from a piece of plate glass.* This could be used alone; but as at first it was thought necessary to have a web, serving as a fixed mark to which the bands could be referred, the rod was treated as the object-glass of a compound cylindrical microscope, the eyepiece being a commercial cylindrical lens of $1\frac{1}{4}$ in. (31 m.m.) focus. Both lenses were mounted on adjustable stands, so that the cylindrical axes could be made accurately vertical, or, rather, accurately parallel to the length of the original

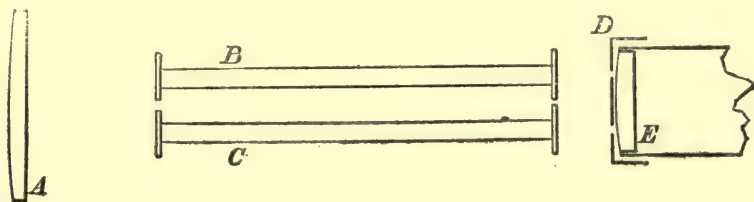


FIG. 1.

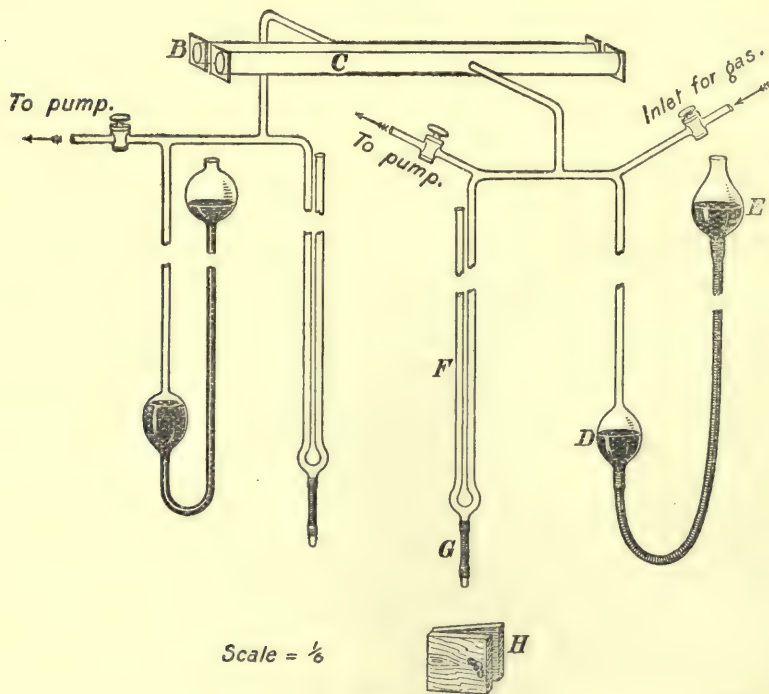


FIG. 2.

and can be brought back to the original position only by abolishing the relative retardation.

When the object is merely to see the interference bands in full perfection, the use of a telescope is not required. The function of the telescope is really to magnify the slit system (*Brit. Assoc. Report*, 1893, p. 703), and this is necessary when, as here, it is desired to operate separately upon the two portions of light. The apparatus is, however, extremely simple, the principal objection to it being the high magnifying power required, leading under ordinary arrangements to a great attenuation of light. I have found that this objection may be almost entirely overcome by the substitution of cylindrical lenses, magnifying

slit. The light from an ordinary paraffin lamp now sufficed, although the magnification was such as to allow the error of setting to be less than $1/20$ of a band interval. It is to be remembered that with this arrangement the various parts of the length of a band correspond, not to the various parts of the original slit, but rather to the various parts of the object-glass. This departure from the operation of a spherical eyepiece is an advantage, inasmuch as optical defects show themselves by deformation of the bands instead of by a more injurious en-

* Preliminary experiments had been made with ordinary glass cane and with tubes charged with water.

croachment upon the distinction between the dark and bright parts.

The collimating lens A (Fig. 1) is situated 23 feet (7 metres) from the source of light. B, C are the tubes, one containing dry air, the other the gas to be experimented upon. They are 1 ft. (30.5 c.m.) long, and of $\frac{1}{2}$ in. (1.3 c.m.) bore, and they are closed at the ends with small plates of parallel glass cut from the same strip. E is the object-glass of the telescope, about 3 in. (7.6 c.m.) in diameter. It is fitted with a cap, D, perforated by two parallel slits. Each slit is $\frac{1}{4}$ in. (6 m.m.) wide, and the distance between the middle lines of the slits is $1\frac{1}{2}$ in. (38 m.m.).

The arrangements for charging the tubes and varying the pressures of the gases are sketched in Fig. 2. A gas pipette, D E, communicates with the tube C, so that by motion of the reservoir E and consequent flow of mercury through the connecting hose, part of the gas may be transferred. The pressure was measured by a U-shaped manometer, F, containing mercury. This was fitted below with a short length of stout rubber tubing, G, to which was applied a squeezer, H. The object of this attachment was to cause a rise of mercury in both limbs immediately before a reading, and thus to avoid the capillary errors that would otherwise have entered. A similar pipette and manometer were connected with the air-tube B. In order to be able, if desired, to follow with the eye a particular band during the changes of pressure (effected by small steps and alternately in the two tubes), diminutive windlasses were provided by which the motions of the reservoirs (E) could be made smooth and slow. In this way all doubt was obviated as to the identity of a band; but after a little experience the precaution was found to be unnecessary.

The manner of experimenting will now be evident. By adjustment of pressures the centre of the middle band was brought to a definite position, determined by the web or otherwise, and the pressures were measured. Both pressures were then altered and adjusted until the band was brought back precisely to its original position. The ratio of the changes of pressure is the inverse ratio of the refractivities ($\mu - 1$) of the gases. The process may be repeated backwards and forwards any number of times, so as to eliminate in great degree errors of the settings and of the pressure readings.

During these observations a curious effect was noticed, made possible by the independent action of the parts of the object-glass situated at various levels, as already referred to. When the bands were stationary, they appeared straight, or nearly so, but when in motion, owing to changes of pressure, they became curved, even in passing the fiducial position, and always in such a manner that the ends led. The explanation is readily seen to depend upon the temporary changes of temperature which accompany compression or rarefaction. The full effect of a compression, for example, would not be attained until the gas had cooled back to its normal temperature, and this recovery of temperature would occur more quickly at the top and bottom, where the gas is in proximity to the metal, than in the central part of the tube.

The success of the measures evidently requires that there should be no apparent movement of the bands apart from real retardations in the tubes. As the apparatus was at first arranged, this condition was insufficiently satisfied. Although all the parts were carried upon the walls of the room, frequent and somewhat sudden displacements of the bands relatively to the web were seen to occur, probably in consequence of the use of wood in some of the supports. The observations could easily be arranged in such a manner that no systematic error could thence enter, but the agreement of individual measures was impaired. Subsequently a remedy was found in the use of a second system of bands, formed by light which passed just above the tubes, to which, instead of to the web, the movable bands were referred. The coincidence of the two systems could be observed with accuracy, and

was found to be maintained in spite of movements of both relatively to the web.

In the comparisons of argon and air (with nearly the same refractivities) the changes of pressure employed were about 8 in. (20 c.m.), being deductions from the atmospheric pressure. In one observation of July 26, the numbers, representing suction in inches of mercury, stood—

Argon.	Air.
8.54	9.96
0.01	1.77
8.53	8.19

$$\text{Ratio} = 0.961,$$

signifying that 8.53 inches of argon balanced 8.19 inches of dry air. Four sets, during which the air and argon (from the globe as last filled for weighing) were changed, taken on July 17, 18, 19, 26, gave respectively for the final ratio 0.962, 0.961, 0.961, 0.960, or as the mean—

$$\frac{\text{Refractivity of argon}}{\text{Refractivity of air}} = 0.961.$$

The evidence from the refractivities, as well as from the weights, is very unfavourable to the view that argon is an allotropic form of nitrogen such as would be denoted by N₃.

The above measurements, having been made with lamp-light, refer to the most luminous region of the spectrum, say in the neighbourhood of D. But since no change in the appearance of the bands at the two settings could be detected, the inference is that the dispersions of the two gases are approximately the same, so that the above ratio would not be much changed, even if another part of the spectrum were chosen. It may be remarked that the displacement actually compensated in the above experiments amounted to about forty bands, each band corresponding to about $\frac{1}{2}$ in. (5 m.m.) pressure of mercury.

Similar comparisons have been made between air and helium. The latter gas, prepared by Professor Ramsay, was brought from London by Mr. W. Randall, who further gave valuable assistance in the manipulations. It appeared at once that the refractivity of helium was remarkably low, 13 in. pressure of the gas being balanced by less than 2 in. pressure of air. The ratios given by single comparisons on July 29 were 0.147, 0.146, 0.145, 0.146, mean 0.146; and on July 30 0.147, 0.147, 0.145, 0.145, mean 0.146. The observations were not made under ideal conditions, on account of the smallness of the changes of air pressure; but we may conclude that with considerable approximation—

$$\frac{\text{Refractivity of helium}}{\text{Refractivity of air}} = 0.146.$$

The lowest refractivity previously known is that of hydrogen, nearly 0.5 of that of air.

Viscosity of Argon and Helium.

The viscosity was investigated by the method of passage through capillary tubes. The approximate formula has been investigated by O. Meyer (*Pogg. Ann.*, cxxvii., p. 270, 1866), on the basis of Stokes's theory for incompressible fluids. If the driving pressure ($p_1 - p_2$) is not too great, the volume V_2 delivered in time t through a tube of radius R and length λ is given by—

$$V_2 = \pi t \frac{p_1^2 - p_2^2}{2p_2} \frac{R^4}{8\eta\lambda},$$

the volume being measured at the lower pressure p_2 , and η denoting the viscosity of the gas. In the comparison of different gases V_2 , p_1 , p_2 , R , λ may be the same, and then η is proportional to t .

In the apparatus employed two gas pipettes and manometers, somewhat similar to those shown in Fig. 2, were connected by a capillary tube of very small bore and

about 1 metre long. The volume V_2 was about 100 c.c., and was caused to pass by a pressure of a few c.m. of mercury, maintained as uniform as possible by means of the pipettes. There was a difficulty, almost inherent in the use of mercury, in securing the right pressures during the first few seconds of an experiment; but this was not of much importance as the whole time t amounted to several minutes. The apparatus was tested upon hydrogen, and was found to give the received numbers with sufficient accuracy. The results, referred to dry air, were for helium 0.96, and for argon 1.21, somewhat higher than for oxygen, which at present stands at the head of the list of the principal gases.

Gas from the Bath Springs.

In the original memoir upon argon (Rayleigh and Ramsay, *Phil. Trans.*, vol. clxxxvi., p. 227, 1895) results were given of weighings of the residue from the Bath gas after removal of oxygen, carbonic anhydride, and moisture, from which it appeared that the proportion of argon was only one-half of that contained in the residue, after similar treatment, from the atmosphere. After the discovery of helium by Professor Ramsay, the question presented itself as to whether this conclusion might not be disturbed by the presence in the Bath gas of helium, whose lightness would tend to compensate the extra density of argon.

An examination of the gas which had stood in my laboratory more than a year, having shown that it still contained no oxygen, it was thought worth while to remove the nitrogen so as to determine the proportion that would refuse oxidation. For this purpose 200 c.c. were worked up with oxygen until the volume, free from nitrogen, was reduced to 8 c.c. On treatment with pyrogallol and alkali, the residue measured 3.3 c.c., representing argon, and helium, if present. On sparking the residue at atmospheric pressure, and examining the spectrum, it was seen to be mainly that of argon, but with an unmistakable exhibition of D_3 . At atmospheric pressure this line appears very diffuse in a spectroscopic of rather high power, but the place was correct.

From another sample of residue from the Bath gas, vacuum tubes were charged by my son, Mr. R. J. Strutt, and some of them showed D_3 sharply defined and precisely coincident with the line of helium in a vacuum tube prepared by Professor Ramsay.

Although the presence of helium in the Bath gas is not doubtful, the quantity seems insufficient to explain the low density found in October, 1894. In order to reconcile that density with the proportion of residue ($3.3/200 = 0.0165$) found in the experiment just described, it would be necessary to suppose that the helium amounted to 25 per cent of the whole residue of argon and helium. Experiment, however, proved that a mixture of argon and helium, containing 10 per cent of the latter gas, showed D_3 more plainly than did the Bath residue. It is just possible that some of the helium was lost by diffusion during the long interval between the experiments whose results are combined in the above estimate.

Buxton Gas.

Gas from the Buxton springs, kindly collected for me by Mr. A. McDougall, was found to contain no appreciable oxygen. The argon amounted to about 2 per cent of the volume. When its spectrum was examined, the presence of D_3 was suspected, but the appearance was too feeble to allow of a definite statement being made. The proportion of helium is in any case very much lower than in the Bath gas.

Is Helium contained in the Atmosphere?

Apart from its independent interest, this question is important in connection with the density of atmospheric argon. Since the spectrum of this gas does not show the line D_3 , we may probably conclude that the proportion of helium is less than 3 per cent; so that there would be

less than 3×10^{-4} of helium in the atmosphere. The experiment about to be described was an attempt to carry the matter further, and is founded upon the observation by Professor Ramsay, that the solubility of helium in water is only 0.007, less than one-fifth of that which we found for argon (*Phil. Trans.*, vol. clxxxvi., p. 225, 1895).

It is evident that if a mixture of helium and argon be dissolved in water until there is only a small fraction remaining over, the proportion of helium will be much increased in the residue. Two experiments have been made, of which that on October 6, 1895, was the more elaborate. About 60 c.c. of argon were shaken for a long time with well boiled water contained in a large flask. When the absorption had ceased, the residue of 30 c.c. was sparked with a little oxygen until no nitrogen could be seen in the spectrum. It was then treated a second time with boiled water until its volume was reduced to $1\frac{1}{2}$ c.c. With this vacuum tubes were charged by my son at two different pressures. In none of them could D_3 be detected; nor was there any marked difference to be seen between the spectra of the washed and the unwashed argon. If helium be present in the atmosphere, it must be in very small quantity, probably much less than a ten-thousandth part.

ON THE OXIDATION OF SOME GASES WITH PALLADINISED COPPER OXIDE.*

By E. D. CAMPBELL.

(Concluded from p. 53).

IN the case of easily burned gases, like hydrogen and carbon monoxide, it is not found necessary to re-oxidise the tube after each combustion, but in the case of more difficultly burned gases this was found desirable, especially when burning at the higher temperatures and when the previous combustion had removed a good deal of oxygen.

In the table all the quantitative combustions were performed with palladinised copper oxide, prepared by the first method, the ignition-point only of the various gases being determined with pure copper oxide in order to determine to what extent the presence of 1 per cent of palladium affected the temperature at which combustion commenced. In the calculation of the rate of combustion of ethylene and of propylene (experiments 18—25 and 28—34), the volume was calculated from the amount of carbon dioxide, since, owing to the use of phosphorus pentoxide in one arm of the U-tube used for collecting the water, there was slight polymerisation, which made the amount of water a little higher than the true value. On the other hand, in the case of isobutylene (experiments 37—41) the rate of combustion was calculated from the amount of water produced, the U-tube being filled with calcium chloride alone, thus avoiding polymerisation. The solubility of isobutylene rendered the carbon dioxide a little in excess of the amount calculated for perfect combustion, so that it was thought to be more accurate in this case to use the weight of water rather than that of carbon dioxide in calculating the rate of combustion.

In all of the gases on which quantitative combustions were made, although a slight excess of unburned gas was forced completely through the train, if the supply was slackened a little, perfect combustion took place and no unburned gas escaped. In the case of methane no combustion took place at 455° , and as 460° was the limit to which nitrogen-filled thermometers could be carried, it was found necessary to lay aside the work so far as the paraffins go until suitable modifications to the furnace can be made by means of which such temperatures as may be necessary for the combustion of these gases can be

* Contributions from the Laboratory of Analytical Chemistry of the University of Michigan. From the *American Chemical Journal*, vol. xvii., No. 9, November, 1895.

Exp. No.	Gas.	Initial combustion pt. with palladium copper oxide.	Initial combustion point with pure copper oxide.	Temp. of combustion. Deg.	Length of time in hrs.	Wt. H ₂ O.	Wt. CO ₂ .	C.c. of gas burned per hr.	Wt. O ₂ removed per hr.
1.	H ₂	80—85	—	—	—	—	—	—	—
2.	H ₂	—	175—180	—	—	—	—	—	—
3.	H ₂	—	—	115—120	6	0.4808	—	99	0.0713
4.	H ₂	—	—	125—130	6	1.295	—	266.4	0.1918
5.	H ₂	—	—	135—140	6	1.974	—	406.2	0.2925
6.	H ₂	—	—	145—150	6	3.544	—	729.2	0.525
7.	H ₂	—	—	165—170	6	3.688	—	754.8	0.5435
8.	CO	100—105	—	—	—	—	—	—	—
9.	CO	—	100—105	—	—	—	—	—	—
10.	CO	—	—	125—130	6	—	0.669	56.4	0.0406
11.	CO	—	—	135—140	6	—	1.0215	86.1	0.062
12.	CO	—	—	145—150	6	—	2.313	196.7	0.1403
13.	CO	—	—	155—160	2½	—	2.101	425.1	0.3059
14.	CO	—	—	175—180	1½	—	1.7685	599.5	0.4292
15.	CO	—	—	195—200	1½	—	1.951	654.9	0.4734
16.	C ₂ H ₄	240—250	—	—	—	—	—	—	—
17.	C ₂ H ₄	—	315—325	—	—	—	—	—	—
18.	C ₂ H ₄	—	—	270—275	2	0.0515	0.116	14.7	0.063
19.	C ₂ H ₄	—	—	295—300	2	0.111	0.268	33.8	0.145
20.	C ₂ H ₄	—	—	325—330	2	0.3215	0.815	103	0.442
21.	C ₂ H ₄	—	—	345—350	2	0.489	1.1725	148.5	0.636
22.	C ₂ H ₄	—	—	370—375	2	0.505	1.3665	172.8	0.741
23.	C ₂ H ₄	—	—	395—400	2	0.5985	1.4555	184	0.789
24.	C ₂ H ₄	—	—	420—425	2	0.742	1.830	231.4	0.993
25.	C ₂ H ₄	—	—	450—455	1½	0.561	1.388	234	1.004
26.	C ₃ H ₆	220—230	—	—	—	—	—	—	—
27.	C ₃ H ₆	—	270—280	—	—	—	—	—	—
28.	C ₃ H ₆	—	—	240—245	2	0.0315	0.0475	4	0.0257
29.	C ₃ H ₆	—	—	270—275	2	0.0905	0.179	15.1	0.0972
30.	C ₃ H ₆	—	—	295—300	2	0.2345	0.569	48	0.3089
31.	C ₃ H ₆	—	—	320—325	2	0.9505	2.332	196.5	1.265
32.	C ₃ H ₆	—	—	345—350	2	1.265	3.092	260.5	1.6695
33.	C ₃ H ₆	—	—	370—375	2	1.2505	3.0125	253.8	1.634
34.	C ₃ H ₆	—	—	395—400	2	1.271	3.0765	259.3	1.668
35.	C ₄ H ₈	270—280	—	—	—	—	—	—	—
36.	C ₄ H ₈	—	320—330	—	—	—	—	—	—
37.	C ₄ H ₈	—	—	270—275	2	0.051	0.196	7.87	0.0755
38.	C ₄ H ₈	—	—	295—300	2	0.185	0.559	28.57	0.2454
39.	C ₄ H ₈	—	—	320—325	2	0.6765	1.8665	104.4	0.895
40.	C ₄ H ₈	—	—	340—345	2	1.6495	4.036	254.8	2.186
41.	C ₄ H ₈	—	—	370—375	¾	1.431	3.4775	588.6	5.059
42.	CH ₄	No combustion at 455°.							

obtained and controlled, when the work will be continued. After obtaining the temperature of ignition and rate of combustion of the ordinary gases occurring in the pure state, mixtures of these gases will be worked upon in order to determine if possible to what extent they may be separated by fractional combustion. The combustion of acetylene differs from that of any of the gases given in the above table, since this gas does not burn at once to carbon dioxide and water, but undergoes a series of rather complex decompositions which would render it incapable of being separated by fractional combustion. In attempting to determine the ignition-point of acetylene, the pure dry grass was passed through a tube containing palladinised copper oxide, having a small tube of anhydrous cupric sulphate attached to the farther end, followed by a U-tube containing calcium hydroxide for the detection of carbon dioxide. A steady flow of gas was kept up through the tube, which was very slowly heated; no apparent change occurred until a temperature of 225°—230° was reached, when the first test for moisture was observed, but no carbon dioxide. The flow of gas was kept up, the temperature of the tube being gradually raised until a temperature of nearly 300° was reached, when the tube was found to be choked up although no test for carbon dioxide had as yet been obtained. On removing the combustion-tube from the furnace the palladinised copper oxide nearest the inlet of the tube was found to be filled for a distance of about 5 c.m. with

a heavy black deposit. The combustion-tube was re-filled with fresh palladinised copper oxide prepared by the second method, heated to nearly 300°, and acetylene once more turned through the tube and the temperature raised, when a test for carbon dioxide was obtained at 315°—320°. On removing the jacket from the furnace a deposit similar to the first was observed, but not in sufficient quantity to choke the tube; this deposit was removed by heating the tube to a red heat, and forcing in oxygen until everything was burned. After thus re-oxidising the tube the jacket was replaced and the temperature raised to and maintained at 345°. Acetylene was turned into the tube at such a rate that 3—5 bubbles per minute passed through the last bulb of the weighed potash bulb used for regular quantitative combustion. This was kept up for two hours, when it was found that the water obtained weighed 0.3171 grm. and the carbon dioxide 0.4834 grm. If combustion had been perfect to carbon dioxide and water, then the amount of water obtained should have been accompanied by 1.547 grms. carbon dioxide, instead of less than one-third this amount. On removing the jacket a deposit similar to the previous ones was observed, which was removed by oxidation at a red heat. A second quantitative combustion was then made, the temperature being 395°—400°. In this combustion the amount of water obtained was 0.4056 grm., accompanied by 1.4753 grms. carbon dioxide—a little greater ratio than the previous one. After removing the jacket the carbon-

aceous deposit was again removed by burning at a red heat, and the water and carbon dioxide produced were weighed. This gave: water, 0.0521 grm.; and carbon dioxide, 0.7737 grm. From these results we see that when acetylene is passed through a tube of palladinised copper oxide at a temperature of 395° – 400° , two-thirds of the carbon and eight-ninths of the hydrogen are oxidised to carbon dioxide and water respectively, while one-third of the carbon and one-ninth of the hydrogen remain in the tube in a form as yet undetermined.

In a combustion similarly conducted, but with the temperature at 445° – 450° , the amount of water obtained in the same length of time was 0.6747 grm., accompanied by 1.9486 grms. of carbon dioxide, thus showing that while the rate at which dissociation took place increased with rise in temperature, oxidation did not seem to reach a higher limit than at 400° .

Credit is due Messrs. R. F. Flintermann, C. R. Rose, and E. B. Hart for the care with which they have carried out the laboratory work of the above research.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 68.)

I SHALL describe farther on the spectrum of the sulphate after it was dried under a bell-jar.

At least two-thirds of the sulphate of calcium, still damp, were gradually put into a large quantity of dilute sesqui-carbonate of ammonium, in a large covered platinum retort. These bodies were left together for twelve hours, taking care to shake the vessel which held them, from time to time. I then washed the carbonate by decantation. For the first five washings I used a very weak solution of sesqui-carbonate of ammonium, and finished with pure water. The washings were repeated so long as the water decanted, when filtered and evaporated down to nine-tenths of its volume, gave a precipitate with a barium solution. After the washing, the carbonate was put into a litre of water, through which was passed carbonic acid to saturation. The supernatant liquid, having settled, was decanted, and the carbonate was twice washed with pure water, then put again into 4 litres of pure water, through which was passed carbonic acid to saturation.

The clear supernatant liquid was gradually brought to boiling-point in a platinum retort, and replaced by an equal volume of pure water, through which carbonic acid was again passed. Eight litres of solution deposited about *six grms.* of granulated carbonate of calcium. Part of this precipitate, when put at once into a Bunsen flame, on a recently heated platinum-wire loop, did *not* colour it *at all*, and spectrum analysis of the flame only showed *very fleeting* traces of the sodium spectrum, and these were identical with those shown by the flame itself. The carbonate was dried under a bell-jar by sulphuric acid.

The bulk of the carbonate of calcium left in the large covered retort was dried in it on a water-bath, and sheltered from atmospheric dust.

To make carbonate from nitrate of calcium, free from strontium, obtained from arragonite and white marble, I proceeded just as I have described for nitrate from calc-spar, absolutely free from strontium. I can therefore dispense with going into details of this subject.

To resume:—

A. As far as concerns the carbonate of calcium obtained from *Iceland spar*, I made it—

1st. By decomposing the purified chloride yielded by the spar.

2nd. By converting carbonate from chloride into nitrate, and by afterwards precipitating this nitrate by means of bicarbonate of ammonium.

3rd. By converting nitrate into oxalate, and reducing this into carbonate by the action of heat.

4th. By converting nitrate into sulphate, and afterwards transforming this sulphate into carbonate.

5th. By dissolving carbonate from sulphate in water charged with carbonic acid.

B. As regards carbonate of calcium made from *arragonite*, I made it by first transforming this compound into chloride free from iron, manganese, and silica, by precipitating the chloride by means of bicarbonate of ammonium, by dissolving the carbonate of calcium thus formed in nitric acid, and freeing the nitrate from the strontium in it, and finally re-precipitating the nitrate by bicarbonate of ammonium.

C. I made carbonate from *white marble* in exactly the same way that I have described for the carbonate from arragonite.

I converted into *chloride* a certain amount of oxide of calcium made by dissociating pure carbonate, obtained from marble. I took care to free this oxide beforehand from sodium, by heating it in an oxyhydrogen blowpipe. I effected this conversion both by heating the oxide to redness, in a current of dry hydrochloric acid, in a platinum boat inside a porcelain tube, and by melting the same oxide, mixed with a large excess of pure chloride of ammonium, in a platinum crucible, in an oxyhydrogen blowpipe.

A recently heated platinum-wire loop, when dipped into either of the melted chlorides thus made, and put into a Bunsen burner fed with coal-gas, or into a hydrogen flame, at once colours the flame yellow, and the colour due to calcium appears only after several moments. The sodium spectrum appears strongly until the chloride is almost entirely reduced to the form of oxychloride. Every attempt I have made to obtain chloride of calcium, which would not show the sodium line on spectrum analysis, failed absolutely.

When carrying on these researches, I had to bear in mind the strong tendency of chloride to combine with sodium. Having left some melted chloride of calcium, still in the boat or platinum crucible, under a glass bell-jar, carefully sheltered from atmospheric dust, it—by attracting the moisture of the air *very slowly* and *becoming liquid*—produced a solution which, when put into a Bunsen flame, gave it the colour due to sodium only, although, on spectrum analysis, I saw both the sodium and calcium spectra.

I have further noticed that, when leaving the solution of chloride in the air, under a bell-jar again, until it absorbed all the moisture it could from the air,—and this takes months to accomplish,—a time came when, on putting it into a Bunsen flame, the solid chloride itself gave it an intense yellow colour, and continued to give it this colour until the magnificent calcium spectrum, seen at the same time as the sodium line, had almost disappeared.

I repeated these experiments many times, and always with the same results. I have already mentioned that the same facts occur both with pure oxide of lithium when converted into chloride, and with chloride of lithium when left in air under a bell-jar.

Chlorides of calcium and lithium, by attracting moisture from the air, thus combine with sodium. I maintain that very hygroscopic bodies are similar to all surfaces the temperature of which is below dew-point, for they, by condensing moisture from the air on themselves, collect sodium at the same time. My study of water of condensation from air on to polished platinum, the results of which I have described in my "*Essai sur la Nature et la Quantité des Matières Minérales existant dans l'Air*," appears to me to render this explanation very feasible.

In any case, I do not think any chemist will be able to determine the weight of sodium combined thus with solid or liquid chloride of calcium, or say in what form the sodium exists in the chloride. And yet chloride of calcium which has been allowed to absorb moisture from the

atmosphere gives to flames the colour due to a sodium compound only.

These facts show how contrary to experience and reason it would be to attribute to a dissociation of the metal calcium or lithium, the presence of the sodium line shown by spectrum analysis in the cases mentioned.

Chemists will readily understand that I did not prepare all the products I have just mentioned at the same time. I will even say that they were prepared at very different times, modifying the methods as experience showed me fresh causes of error. These methods constitute the whole of my researches, and the means of reaching the end I had in view, which was to ascertain whether it was possible to obtain oxide of calcium of uniform composition, no matter what its origin.

I return to the characteristics of the different samples of carbonate of calcium, and the single sample of sulphate of calcium.

All these products, immediately after their production,—that is, whilst still moist, and above all before coming in contact with the air, to be dried,—when put into a Bunsen flame, gave it a *very transient* yellow colour, excepting the sulphate and the carbonate which was precipitated, by boiling, from the solution in water containing carbonic acid. In the oxyhydrogen blowpipe this colour disappeared almost at once, and was replaced by the colour due to calcium. The calcium spectrum appears the same in all, as it is described in the next chapter, without a trace of the sodium spectrum with the sulphate and the carbonate which was dissolved in water containing carbonic acid, and with transient traces of this spectrum with the other carbonates.

Without any exception, all the compounds of calcium which were dried in the platinum vessels in which they were made, or out of these vessels, but in contact with air, free from dust, instantly gave to flames the colour due to sodium, and showed the sodium spectrum until, by means of the oxyhydrogen blowpipe, all the sodium was eliminated.

The influence of the air is therefore of as much importance as that of the methods used to form these calcium compounds.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 16th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 70).

2. "The Action of Sodium Alcoholate on certain Aromatic Amides." By J. B. COHEN, Ph.D., and W. H. ARCHDEACON, B.Sc.

If acetanilide is dissolved in ether, and sodium methylate added, a crystalline addition compound of the formula $\text{Ph}\cdot\text{NH}\cdot\text{Ac}\cdot\text{CH}_3\cdot\text{ONa}$ is formed.

Similar compounds with sodium methylate and ethylate have been prepared from ortho- and para-acetoluide, α - and β -acetonaphthalide, benzanilide, and formanilide.

With formylphenylhydrazide, disodium formylphenylhydrazide is obtained. Benzamide yields a sodium compound of indefinite composition.

With propionanilide and butyranilide compounds similar to acetanilide sodium alcoholate appear to be formed in solution, but they could not be isolated. Sodium alcoholate does not react with diphenylacetamide and ethylacetanilide.

3. "Note on the Electrolytic Conductivity of Formanilide and Thioformanilide." By THOMAS EWAN, B.Sc., Ph.D.

The majority of the amides are too little soluble in

water to allow of measurements of electrolytic conductivity being made. Others, again, are decomposed by water too rapidly into acid and amine. The conductivity of formanilide shows that it possesses feebly acidic properties. In aqueous solution the sodium compound of formanilide is completely decomposed. In the case of thioformanilide, the sodium compound appears to exist in aqueous solution.

4. "The Action of Sugar on Ammoniacal Silver Nitrate." By J. HENDERSON, B.Sc.

The author has investigated the reducing powers of the following substances on ammoniacal silver nitrate, viz., glucose, lævulose, galactose, cane-sugar, starch, dextrin, lactose, and maltose. The results obtained may be thus summarised:—

1. When glucose, levulose, and galactose are heated with ammoniacal silver nitrate under the given conditions, a definite factor can be found in each case.

2. Cane-sugar, starch, and dextrin, when heated under the same conditions, exert no reducing action on ammoniacal silver nitrate.

3. In the case of lactose and maltose a definite factor cannot be obtained, owing to the gradual hydrolysis of the disaccharide by the ammonia.

5. "Solution and Diffusion of Certain Metals in Mercury." By W. J. HUMPHREYS.

The author has examined quantitatively the solution and diffusion of tin, lead, bismuth, zinc, copper, and silver in mercury with a view to determining the extent to which these phenomena differ, if at all, from the solution and diffusion of non-metallic solids in liquids. Pieces of metal were placed on the upper surface of a column of pure mercury, and samples of the liquid were taken at definite depths below the surface, and the amount of foreign metal estimated. As far as the experiments go, the author concludes that the solution and diffusion of metals in mercury do not essentially differ from those of non-metallic solids in liquids. Copper and silver dissolve in mercury to a very small extent at ordinary temperatures, but diffuse very rapidly.

6. "On some of the Ethereal Salts of Active and Inactive Monobenzoyl, Dibenzoyl, Diphenylacetyl, and Dipropionyl Glyceric Acids." By PERCY FRANKLAND, Ph.D., F.R.S., and JOHN MACGREGOR, M.A.

The following compounds have been prepared by the authors:—

Methyl dibenzoylglycerate (active). Long radiating needles melting at $58-59^\circ$.

$[\alpha]_D$ at $183^\circ = +8.55^\circ$; $d_{183^\circ/4^\circ} = 1.0951$.

" $59.5^\circ = +22.13^\circ$; $d_{59.5^\circ/4^\circ} = 1.1877$.

" 15° (calculated) = $+26.89^\circ$.

Methyl dibenzoylglycerate (inactive). Long radiating needles melting at 44.46° .

Ethyl dibenzoylglycerate (active). Radiating needles melting at 25° .

$[\alpha]_D$ at $183^\circ = +8.62^\circ$; $d_{183^\circ/4^\circ} = 1.0599$.

" 16.5° (superfusion) = $+26.28^\circ$; $d_{16.5^\circ/4^\circ} = 1.1996$.

" 15° (calculated) = $+26.58^\circ$.

Propyldibenzoylglycerate (active). Liquid boiling at $267-269^\circ$ under 11 m.m. pressure.

$[\alpha]_D$ at $87^\circ = +15.34^\circ$; $d_{87^\circ/4^\circ} = 1.1175$.

" $19.5^\circ = +20.71^\circ$; $d_{19.5^\circ/4^\circ} = 1.1771$.

" 15° (calculated) = $+21.00^\circ$.

Methyl diphenylacetyl glycerate (active). Liquid boiling at $266-270^\circ$ under 17 m.m.

$[\alpha]_D$ at $77.5^\circ = -14.10^\circ$; $d_{77.5^\circ/4^\circ} = 1.1427$.

" $14.5^\circ = -16.06^\circ$; $d_{14.5^\circ/4^\circ} = 1.1972$.

Methyl monobenzoylglycerate (active). A dextro-rotatory liquid which, on distillation, yielded a more

dextro-rotatory distillate. It is probable that the original liquid consisted of the α - and β -isomeric monobenzoylglycerates, of which the α -compound would have the lower boiling-point, and that this α -compound is more dextro-rotatory than the β -compound.

Methyl monobenzoylglycerate (inactive). Crystallises in small warty groups melting at $92.5-93^\circ$. It is probable that this is the β -compound, the α -compound being liquid.

Ethyl monobenzoylglycerate (active). Radiating needles melting at 62° . This is probably the β -compound; it is laevorotatory, whilst the liquid from which it crystallised, and which would contain the α -compound, was dextro-rotatory. This solid ethyl monobenzoylglycerate is remarkable for its almost complete insensitiveness to temperature, thus—

$$[\alpha]_D \text{ at } 13.65^\circ = -9.47^\circ; d \ 13.65^\circ/4^\circ = 1.0886.$$

$$,, \quad 67^\circ = -9.80^\circ; d \ 67^\circ/4^\circ = 1.1547.$$

Methyl dipropionylglycerate (active). Liquid.

$$[\alpha]_D \text{ at } 15^\circ = -10.97^\circ; d \ 15^\circ/4^\circ = 1.1349.$$

The relationship between the rotatory power and the chemical constitution of these and other derivatives of glyceric acid is discussed, attention being again directed to the manner in which the rotation is more powerfully influenced by the qualitative character than by the mere mass of the groups attached to the asymmetric carbon atom. It is also pointed out that the reaction is more influenced by an element or group of elements introduced in the vicinity than by the same at a distance from the asymmetric carbon atom.

7. "On the Rotation of Optically Active Compounds in Organic Solvents." By PERCY FRANKLAND, Ph.D., F.R.S., and R. H. PICKARD, B.Sc.

The authors have investigated the variation in the value of $[\alpha]_D$ for methyl dibenzoylglycerate when dissolved in benzene, nitrobenzene, ethylene dibromide, and acetic acid respectively, employing a number of different concentrations in the case of each solvent. The molecular weight was also cryoscopically determined for a series of similar concentrations with each solvent.

The cryoscopic determinations showed that inactive methyl dibenzoylglycerate does not exist as a "racemised" molecule in these solvents, practically the same values for the molecular weight being obtained as with the active compound under the same conditions.

The cryoscopic values were, with all the concentrations employed, below the theoretical ones in benzene; in ethylene dibromide and nitrobenzene they were below the theory with dilute, and above the theory with strong solutions. In the case of acetic acid, the cryoscopic values were with all concentrations sometimes above, and sometimes below, the theoretical value.

The values of $[\alpha]_D$ in the benzene solutions were much in excess, whilst in the nitrobenzene and ethylene dibromide solutions they were much below the value for $[\alpha]_D$ exhibited by the pure substance; in acetic acid the values for $[\alpha]_D$ most closely approximated to that of the pure substance. Low cryoscopic values for the molecular weight of methyl dibenzoylglycerate were accompanied by high values for $[\alpha]_D$, and vice versa.

This relationship between $[\alpha]_D$ and indicated molecular weight is borne out by the behaviour of ethyl diacetyl-glycerate in benzene and acetic acid solutions respectively, only that in this case the low molecular weights and high specific rotations were obtained in acetic acid, the high molecular weights and low rotations in benzene solution.

The real value of $[\alpha]_D$ for an active body cannot be directly calculated from the rotation of its solution, even when the cryoscopic examination of that solution shows the molecular weight to be normal, and even a moderately accurate estimate of the real value of $[\alpha]_D$ can only be arrived at by the study of solutions giving normal molecular weights and extrapolating for infinite concentration on their rotation curves.

The explanation of these phenomena on the assumption of dissociation and association processes taking place in the several solutions, as has been suggested by Freundler, is discussed. The dissociation indicated by the low cryoscopic values obtained with methyl dibenzoylglycerate in benzene, and with ethyl diacetyl-glycerate in acetic acid solution, appears to be in harmony with the rotation phenomena only if the dissociation consists in the splitting off of the methyl and ethyl groups respectively, the active ion retaining in each case the acid radicles (benzoyl and acetyl). This conclusion is opposed to that arrived at by Freundler in the case of the diacyl tartrates.

8. "Note on the Action of Hydrogen Chloride on Ethyl Alcohol." By J. C. CAIN, B.Sc., Ph.D.

The author refers to the statement recently made by Dr. Armstrong, in his presidential address to the Society, that "Perkin has established the incorrectness of the supposition that until recently has always been made, that hydrogen chloride, when dissolved in alcohol, acts fairly readily on it," and points out that this supposition has been known to be incorrect for a considerable time.

Berthelot, in 1880, found that no reaction takes place on making the solution, and Villiers found a reaction at $10-25^\circ$ only after some months. The author examined the action of hydrogen chloride on ethyl alcohol in 1893, and found that hydrogen chloride had no action on ethyl alcohol after acting for seventeen days at 0°C ., or for fifteen days at 15°C . The reaction probably begins at $20-25^\circ\text{C}$.

A saturated solution of hydrogen chloride in alcohol contains 39.06 per cent HCl, at 10°C . This is near the number found by Dr. W. H. Perkin, sen. (38.45 per cent). The temperature at which the experiment was made is not given, and was therefore probably higher than 10°C .

9. "Transformation of the Alkylammonium Cyanates into the corresponding Ureas." By J. WALKER and J. R. APPELYARD.

A comparison has been made of the rates of transformation of the alkylammonium cyanates into ureas, and of the reverse transformation of the ureas into cyanates. In every case the results agree with the assumption that the cyanates are present in the aqueous solution in the form of two independent ions. In some instances the reverse transformation is well developed; for example, equilibrium is reached in a $1/15$ normal solution of tertiary amyl ammonium cyanate when half of the cyanate has been transformed into tertiary amyl urea, no production of the urea beyond that amount taking place. No definite relation between the values of the constants and the nature and number of the replacing alkyl groups was observed.

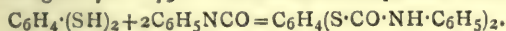
10. "On certain Phenylthiocarbamates." By H. LLOYD SNAPE, D.Sc., Ph.D.

The author has examined the action of phenylthiocarbimide upon phenol, resorcinol, quinol, and glycol. A. E. Dixon (*Trans.*, 57, 268) had already shown that interaction takes place between the above-named thiocarbimide and phenol; but his paper had been overlooked by the writer, who claims, in the course of the experiments he independently carried out, to have obtained the phenyl salt of phenylthiocarbamic acid in purer condition and in larger quantity. He found, in opposition to Dixon's experience, that the higher the temperature (below 280°) and the longer the duration of the experiment, the better was the yield, and in one experiment found this to amount to 25 per cent of the theoretical, whereas Dixon, working at lower temperatures and for a shorter time, only obtained 7 per cent. By crystallisation from absolute alcohol, the crystals obtained melted sharply at 148° ($149^\circ-151^\circ$, Dixon).

So much difficulty having been experienced in effecting combination between phenylthiocarbimide and phenol, it was to be anticipated that reaction between the former substance and dihydroxy-compounds would be even more difficult to carry out; and no thiocarbamate could be

obtained from resorcinol, quinol, or glycol. The writer, however, succeeded in obtaining, by the action of phenylcyanate upon dithioresorcinol and dithioquinol respectively, the isomerides of the thiocarbamates he had hoped to prepare by the foregoing method.

m-Phenylene Salt of Phenylenethiocarbamic Acid.—Phenylcyanate and dithioresorcinol, in the theoretical proportions, were heated in a bath containing a solution of common salt for half an hour. Crystals rapidly separated. After washing with cold alcohol and re-crystallisation from glacial acetic acid, large white needles were obtained, melting at 178° — 179° . The reaction is expressed thus—



p-Phenylene Salt of Phenylenethiocarbamic Acid.—Phenylcyanate and dithioquinol was heated in a water bath. Again combination readily occurred. The crystals obtained by re-crystallisation from glacial acetic acid were smaller than in the preceding case, and melted at 200° — 202° .

II. The Available Potash in Soils. By T. B. WOOD M.A.

The author has had under his care a number of experimental plots in Norfolk and Suffolk, and in this paper he tests the practicability of Dr. Bernard Dyer's method of estimating available potash in soils (*Trans.*, 1894, 115—167), by comparing the analytical numbers obtained by Dr. Dyer's method with the results obtained in actual field experiment.

The soils experimented upon may be divided into two classes, viz., (1) those rich in available potash and (2) those poor in this substance. The former soils gave no marked crop increase (barley) when treated with potash manures, the latter gave a very large increase.

The former soils gave by Dr. Dyer's method on an average 0.0147 per cent of available potash (sol. in 1 per cent citric acid), the latter only 0.0073 per cent, whereas the potash soluble in strong hydrochloric acid (0.178 and 0.137) was much more nearly equal in each case.

The author concludes that Dr. Dyer's method is likely to be of technical value to the agriculturist; since, in the cases examined, laboratory experiments lead to the same conclusions as the more tedious and expensive field experiments. The modification of the method mentioned at the end of Dr. Dyer's paper for use in the case of soils containing much chalk gives far less satisfactory results than the unmodified analytical process.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 3, January 20, 1896.

Action of Carbonyl Chloride upon some Hydrogenous Compounds.—A. Besson.—The author has experimented on phosphonium bromide, phosphonium iodide, dry hydrogen phosphide, PH_3 , and hydrogen sulphide and selenide.

Dichloralglucose in Monochloralglucosane.—J. Meunier.—Dichloralglucosane, $\text{C}_6\text{H}_{16}\text{O}_4(\text{OC}_2\text{Cl}_3)_2$, crystallises in white needles insoluble in water, soluble in 300 parts of alcohol and 45 parts of ether at 20° . It is fusible at 225° , and resists the action of acids. Monochloralglucosane, $\text{C}_6\text{H}_{14}\text{O}_4(\text{OC}_2\text{Cl}_3)$, forms nacreous lamellæ, fusible at 225° , insoluble in water and cold alcohol, soluble in boiling alcohol, but re-deposited on cooling; soluble in 1000 parts of ether; not attacked by acids

Bulletin de la Société Chimique de Paris.

Series 3, Vols. xiii.-xiv., No. 15, 1895.

Researches on the Mercurous Salts.—Raoul Varet.—A thermochemical paper treating of the mercurous nitrate, sulphate, acetate, chloride, bromide, iodide, and oxide.

Alcohols derived from a Dextro-terebenthene: Eucalyptene.—G. Bouchardat and M. Tardy.

Isocampholic Acid.—M. Guerbet.—An account of the salts and the ethers of isocampholic acid.

Detection of Cotton Oil in American Lards.—J. Dupont.—The author points out that lards of American origin differ from European samples both as regards the indices of refraction taken with the oleo-refractometer, the iodine figure, and the action with silver nitrate.

Analysis of Lard and of similar Fats: Detection of Vegetable Oils.—Ferdinand Jean.—Vegetable oils, if added to lard, &c., increase the density, raise the iodine figure, lower the melting-point, the standard of fatty acids, Koerstorffer's number, and diminish the optical deviation. With the oleo-refractometer all the vegetable oils reflect to the right-hand of zero; hence lards mixed with vegetable oils show a deviation less than -12.5 , the normal deviation of pure lard. The animal fats change the density little, but lower the iodine figure, raise the melting-point and the standard of the fatty acids, increase Koerstorffer's number and the optical deviation of the oleorefractometer beyond -12.5° .

Revue Universelle des Mines et de la Metallurgie.

Series 3, Vol. xxxii., No. 2.

Congress on Building Materials.—In September last a Congress was held at Zurich to agree upon methods for the examination of building materials. The meeting seems to have confined itself simply to metals, though stone, cements, timber, paper, and protective coatings, each require separate study. A number of industrialists were present, from Germany, Austria, France, and Russia. Belgium, Britain, and America were scarcely represented. An International Association for the assay of building materials was organised; A Congress will be held at Stockholm in the course of 1897.

MEETINGS FOR THE WEEK.

MONDAY, 17th.—Society of Arts, 8. (Cantor Lectures). "Chemistry of certain Metals and their Compounds used in Building, and the Changes produced in them by Air, Moisture, and Noxious Gases, &c.," by Prof. J. M. Thomson, F.R.S.E.

Medical, 8.30.

TUESDAY, 18th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.

Society of Arts, 8. "The Development of Electrical Traction Apparatus," by H. F. Parshall.

Institute of Civil Engineers, 8.

Pathological, 8.30.

Photographic, 8.

WEDNESDAY, 19th.—Society of Arts, 8. "Report of the Royal Commission on Secondary Education," by H. Macan.

Meteorological, 7.30.

Microscopical, 8.

THURSDAY, 20th.—Royal, 4.30.

Royal Society Club, 6.30.

Royal Institution, 3. "Some Aspects of Modern Botany," by Prof. H. Marshall Ward, F.R.S.

Chemical, 8. "Origin of Colour—the Yellow 2-3-Hydroxynaphthoic Acid;" "Note on Etherification;" "The Relation of Pinene to Citrene;" by Prof. Armstrong, F.R.S.

FRIDAY, 21st.—Royal Institution, 9. "The Past, Present, and Future Water Supply of London," by Dr. E. Frankland, F.R.S.

Quekett Club, 8. (Anniversary).

Geological, 3. (Anniversary).

SATURDAY, 22nd.—Royal Institution, 3. "Light," by Lord Rayleigh, F.R.S., &c.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1891.

EXPERIMENTS WITH RÖNTGEN'S RAYS.

By ALBERT NODON.

THE voltaic arc produced in the air does not emit to an appreciable extent radiations having the property of traversing opaque substances like the rays of Röntgen.

A sensitive plate (silver gelatino-bromide) infolded in substances opaque to light,—*e. g.*, several thicknesses of black paper, and then exposed for fifteen minutes to the direct radiations of an arc of 20 ampères, at the distance of 0.40 metre, showed on development no sensible impression, whilst under the same circumstances it revealed a very distinct action of Röntgen's rays.

This result seems to demonstrate that the ultra-violet radiations of the spectrum in which the arc is rich do not appreciably traverse opaque substances.

Various coloured media are traversed by Röntgen's rays with equal ease. The experiment was made with a screen of leaf zinc perforated with apertures, before which there were arranged respectively plates of coloured gelatin, which transmitted only very limited portions of the spectrum. One of these apertures was kept open, and another was covered with uncoloured gelatin. After exposure to Röntgen's rays behind a screen of black paper, the photographic plate showed on development equal impressions produced through the various apertures.—*Comptes Rendus*, cxxii., p. 237.

PERMEABILITY OF METALS FOR THE X RAYS.

By V. CHABAUD.

I HAVE examined fourteen common metals or alloys as regards their permeability for the X rays. The results obtained are shown on the photographs which I have the honour of submitting to the Academy.

The metals examined have been rolled out to the thickness of 0.2 m.m., and cut up into rectangular slips 35 m.m. in length and 7 in width, and attached side by side, and in a parallel position, on one and the same cardboard. In addition a slip of platinum, of 1/100th m.m. in thickness, is superimposed as a check, intersecting the other slips transversely.

The sensitive photographic plate was protected against light by a double layer of black paper. The system of metal slips was laid against this paper during the exposure. The time of exposure was forty-five minutes, and the length of the sparks of the exciting coil was 7 c.m.

The metals thus compared were the following:—Lead, zinc, copper, zinc amalgam, tin, steel, gold, silver, aluminium, and platinum.

The experiment showed that, at the thickness of 0.2 m.m., platinum alone is perfectly opaque. Aluminium, as is already known, is very transparent.

The other metals above named are appreciably transparent.

Platinum itself, at the thickness of 1/100th m.m., is easily permeated, since the check band threw a slight shade upon the paper. This shade was seen traversing all those projected by the other metals, which shows their transparency.

Mercury deserves a special place. At the thickness of 0.1 m.m. it appears as opaque as platinum. In order to

obtain a plate of mercury of this thickness, I employed a trough hollowed in wood, 0.1 m.m. in depth, closed with a plate of varnished glass. It remains to be seen if—at the thickness, *e. g.*, of 1/100th m.m.—mercury in turn will appear transparent like platinum.—*Comptes Rendus*, cxxii., p. 237.

THE PHOTOGRAPHY OF METALLIC OBJECTS THROUGH OPAQUE SUBSTANCES, BY MEANS OF THE BRUSH OF AN INDUCTION-COIL WITHOUT A CROOKES TUBE.

By G. MOREAU.

ON repeating Röntgen's experiments on the photography of opaque objects by means of a Crookes tube, I have obtained, through a layer of cardboard of several metres in thickness, distinct proofs of different metallic objects (a steel key, the copper stand of a camera lucida, an aluminium wheel, &c.). All these proofs present the relief of the objects due to shadows, the orientation of which indicate that the active rays seem to come from the positive part of the Crookes tube.

I had the idea of substituting for the Crookes tube the brush of a strong induction-coil, actuated by a medium current of 6 ampères. The brush was produced between a positive point and a small negative plate on one or more negative points.

The sensitive plate was placed, along with the object to be photographed, in the interior of a box of cardboard, completely closed. The box could be placed normally or parallel to the effluve, and separated from it by cardboard, or a plate of wood 0.005 metre in thickness.

A first observation, made with five brushes normal to the box, gave nothing appreciable.

Six other photographs were taken with a parallel brush, and gave negative proofs, quite distinct and very intense.

All these proofs present a maximum of action at the level of the brush. They show thus that, as in the Crookes tube, the active rays come from the positive region of the oscillatory system.

The two photographs taken through wood indicate to me a notable absorption of the rays of a perceptible refraction, which I have not yet had the opportunity of measuring exactly.

The duration of the exposure varied from thirty to sixty minutes, and I hope to be able to reduce it in future, the intensity of the proofs indicating this possibility. I have tried to photograph the above objects with the brush of an electro-static machine. Hitherto I have obtained nothing.—*Comptes Rendus*, cxxii., p. 238.

A VIEW ON ARGON.

THE *Actualité Médicale*, a French medical paper, gives the following article, apparently from the pen of Dr. Foveau de Courmelles:—

Another product which I must be satisfied with mentioning, and the existence of which I had denounced (!) a glance of the mind, is a new body, produced, in my opinion, by atmospheric electricity: it is *ekazote*. Two English scientists have recently signalled the presence in the ambient air, not merely of oxygen and nitrogen, but of *ekazote*, which is for us electrified nitrogen, a companion to *oxone*, or electrified oxygen. In the inaugural lesson of my free course of electro-therapy, at the École Pratique de la Faculté de Médecine de Paris, I said, on April 24th, 1893, "Lightning furrows space, decomposes watery vapour, renders the *nitrogen electrified*, and then are formed ozone, ammonium nitrate, oxygenated water."

This, it will be said, was merely a glance of the mind, or hypothesis. Certainly so. But in Science do we not

commonly proceed by hypothesis and empiricism, the former of course preceding the latter. In the same manner as Leverrier signalled in space the presence of the planet Neptune, which was discovered two years afterwards by a Berlin astronomer.

The writer even suggests that De Romas and Franklin have probably anticipated Lord Rayleigh and Professor Ramsay in the discovery of argon, though without submitting any evidence for his opinion. He insinuates that Rayleigh and Ramsay have set out from the hypothesis—which they have formulated for themselves or heard formulated by some one else—that ozone, electrified oxygen, ought to have a pendant in the form of electrified nitrogen.

EXAMINATION OF WATER.

IN testing the water of wells for possible contamination by the leakage of cesspools, &c., Nördlinger proposes to make use of saprol. This disinfective agent—which contains kresol—can be recognised by its odour, in the proportion of 1 : 1,000,000, and even in dilutions of 1 : 2,000,000 is betrayed by its characteristic taste. We should therefore have to pour saprol into cesspools which are suspected of infecting adjacent wells, and to examine the water of the latter as to its taste and smell.

A colorimetric determination of phosphoric acid in water, available up to a proportion of at most 5 m.grms. phosphoric acid per litre, is performed by Alessandri with the solution of molybdenum. He uses for comparison a solution of 0.1 grm. calcium phosphate in a few drops of nitric acid, which he first makes up to 1 litre, and then dilutes further as may be required. Waters containing a higher proportion of phosphoric acid must be suitably diluted, as otherwise the result is not a mere yellow colouration, but a precipitate. Silica must of course be previously eliminated.

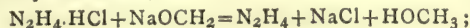
The author mentions a special case in which a high proportion of phosphoric acid does not justify the condemnation of a water, *i.e.*, when it is derived from the fossil remains of primeval animals. Phosphoric acid may be separated from water by ebullition as a calcium salt.—*Zeitsch. f. Analyt. Chem.*, and *Pharm. Central-Halle*.

ON FREE HYDRAZIN.

By C. A. LOBRY DE BRUYN.

HYDRAZIN has been known hitherto only as hydrate (N_2H_6O) and in the form of salts. The hydrate is a liquid which has the constant boiling-point 119° . Its discoverer, Prof. Curtius, has in his latest memoirs expressed the conjecture that the free base is too unstable to exist in the free condition.

The free base may be obtained by two methods: by decomposing the hydrochlorate with sodium methylate in a methylic solution,—



or, secondly, by heating the hydrate with barium oxide to 100° and distilling under reduced pressure.

The following is excerpted from communications published elsewhere (*Ann. d. Chem.*, ccliii., 5, and *Berichte*, xxi., 1810):—Free hydrazin is a liquid boiling without decomposition at 113.5° (761 m.m.). On cooling below zero it solidifies, but melts at $+1.4^\circ$. Its specific gravity is about equal to that of the hydrate, *i.e.*, 1.003 at 23° . It is a very stable substance, and, unlike hydroxylamine and hydrogen peroxide, it is non-explosive. It may be heated without decomposition to above 300° .

With the halogens there is a very violent reaction. With solid sulphur it generates hydrogen sulphide even at common temperatures. Its sharply reductive power is

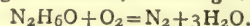
therefore manifested on contact with this element, since, like hydrogen iodide, it gives off its hydrogen to sulphur even at ordinary temperature. It is oxidised by oxygen with liberation of nitrogen, so that the free base cannot be exposed to the air. With sodium it sets up a violent reaction. The base dissolves various salts,—*Berichte*, No. 19.

ON THE PRODUCTION OF CERTAIN OF THE PROPERTIES OF HYDRAZIN HYDRATE.

By C. A. LOBRY DE BRUYN.

ELSEWHERE I have shown that hydrazin hydrate can be conveniently prepared without a special apparatus of silver if the distillation and fractionation are effected at a reduced pressure. If we reduce the temperature to 50° the glass is not attacked. We proceed by distilling off chiefly large quantities of a solution obtained from sulphate and potassa in a tinned copper still (the distillate being fractionated if necessary), an approximately equal quantity of alcohol added to the residue, the potassium sulphate filtered off, and the alcohol is first distilled off from the residue at the ordinary pressure. Dilute solution of hydrate is then added until the temperature has risen to 115° , and the hydrate is, lastly, fractionated at a pressure of 100–150 m.m. We thus obtain a very good yield.

At the pressure of 26 m.m. the hydrate boils at 47° . It is not decomposed on boiling for seven hours. On exposure to the air it is readily oxidised, with a formation of nitrogen. By oxygen it is decomposed quantitatively without a change of volume, according to the equation—



It readily dissolves several salts, *e.g.*, potassium bromide, iodide, and cyanide, ammonium sulphate, barium nitrate, magnesium sulphate, potassa, soda, and gaseous ammonia, but sodium chloride, potassium and lead nitrates less readily.

Sulphur reacts readily with the hydrate, hence vulcanite is easily attacked by the vapours and the liquid. A brownish red liquid is produced containing sulphur and ammonium sulphide in solution.

White phosphorus gradually takes a yellow reddish violet and black colouration, and a faint odour of hydrogen phosphide is perceptible. On dilution with water a black precipitate is deposited, probably a solid hydrogen phosphide. Sodium reacts rather violently with the hydrate. These reactions agree with those of free hydrazin.—*Berichte*, No. 19, January 19, p. 3086.

ON THE YELLOW AUTUMNAL COLOURING-MATTER OF LEAVES.

By G. STAATS.

IT seemed to me interesting to decide whether in the autumnal colouration of leaves the chlorophyll is split up into the two components phylloxanthin and phyllocyanin, and in such a manner that the latter is destroyed whilst the phylloxanthin occasions the yellow colouration of leaves.

On digesting in boiling alcohol the thoroughly yellow leaves of the summer linden (*Tilia euchlora*), we obtain an intensely yellow solution. In order to compare this solution with that of phylloxanthin I decomposed the chlorophyll of the lime-tree and the acacia (*Robinia*) into phylloxanthin and phyllocyanin by the introduction of hydrochloric acid vapours according to Schunck's method. I thus obtained much more phyllocyanin from the chlorophyll of the acacia than from that of the linden. The phylloxanthin from the leaves of both trees showed the red fluorescence of chlorophyll, whilst this phenomenon did not appear in the alcoholic extract of the linden

leaves which had turned yellow in autumn. Hence the autumnal yellow (or, as I propose to call it, autumnixanthin) is not identical with phylloxanthin.

In the boiling, alcoholic solutions of the autumnixanthin of the linden and the hornbeam solution of potassa produced reddish-brown precipitates and yellow solutions. The precipitates are insoluble in ether and alcohol, but soluble in water. Hydrochloric acid dissolves them with a yellow colour. But if we add the solutions of autumnixanthin drop by drop to a little boiling hydrochloric acid, and concentrate as far as possible at a boiling temperature, continuing the addition of the autumnixanthin, we obtain red solutions, which in the case of the linden leaves are of the colour of port wine. The precipitate obtained with potassa lye in a boiling extract of the autumnixanthin of the linden dissolves in water with a splendid garnet-red colour, but it is obtainable only from the solution of large quantities of purely yellow freshly fallen linden leaves. Leaves which have been lying upon the ground for some time, or have been discoloured by frost, yield little red pigment. Such a decrease is not observed with hornbeam leaves. The red potassium compound obtained from the autumnixanthin of the linden crystallises from alcoholic water (at the temperature of a dwelling room) in fine reddish yellow needles, often a m.m. in length. The pigment of beech-autumnixanthin obtained by the same reaction is likewise crystalline.

The splendid red alcoholic extract of the autumnal leaves of the "blood-oak" (*Quercus ruber*) gives the same reaction with potassa lye. On adding the potassa lye the red solution first turns to a chlorophyll-green, and then becomes yellow with the separation of a reddish-brown precipitate, which, as in the above-mentioned reactions, is insoluble in alcohol and ether, but dissolves in water with a reddish-yellow colour.

The precipitates obtained with potassa-lye are soluble in hydrochloric acid when the yellow colour returns.

The potassium reaction seems therefore to take place identically for the pigments of the various leaves as modified by the autumnal change, and forms an appendage to the scission of chlorophyll by alkalis as observed by E. Schunck.

Whether the yellow pigment formed in the autumnal change, which I obtained only in an amorphous state (though some of its compounds crystallise), pre-exists in the green leaves I did not succeed in deciding. In the alcoholic extracts I examined only the compounds of the chlorophyll, or the decoctions of the leaves of the linden, the ash, the beech, and the oak, yielded reddish-yellow solutions, containing tannin. In the reaction-products of autumnixanthin I could not detect any tannin.

Being induced by the experiments of Timiriæzoff, I experimented on the discolouration of the kinds of chlorophyll in the living cell. Nascent hydrogen, acetic acid, and sulphuric acid acted with equal strength on both kinds of chlorophyll. Direct sunlight bleached the acacia chlorophyll—generally very stable—in the living cell with the formation of a flocculent precipitate.—*Berichte*, No. 17, p. 2807.

VOLUMETRIC DETERMINATION OF CHLORO-PLATINATES, DETERMINATION OF POTASSIUM, AMMONIUM, NITROGEN, OR PLATINUM.

IN order to determine the potassium volumetrically with a solution of silver the potassium compound in question is first converted into a chloride. This is effected by precipitating the potassium as a platinum double salt, collecting it, igniting it along with a reducing agent, and extracting the residue with water. F. Mohr remarks concerning this process, that as regards the accuracy of the process it would be advantageous to determine the total chlorine of the platinum double salt. He therefore reduces the

double salt by ignition with sodium oxalate, and extracts the residue with water. L. L. de Koninck proposes to dissolve the double platinum salt in boiling water, and to reduce it with magnesium ribbon. This process, however, still leaves something to be desired in point of accuracy, whence he has subsequently effected the reduction with magnesium in the form of powder, and thus obtains accurate results. Determinations of this method are, however, rendered more difficult by the fact that the magnesium of commerce almost always contains chlorine.

De Koninck further attempted (*Chemiker Zeitung*) to reduce the double platinum salts by formiates, a procedure which had been previously proposed by Corenwinder and Contamine (*Comptes Rendus*). The chloroplatinate, obtained in the usual way, is collected on a filter, washed in alcohol, and dissolved in boiling water or formiate free from chlorine formiate. The author used calcium formiate, which is easily purified by re-crystallisation. The mixture is then heated for some time until the platinum is totally deposited, and the supernatant liquid is perfectly colourless.

The solution is neutralised by the addition of a trace of calcium carbonate, the platinum is filtered off, washed with hot water, and the chlorine is determined in the filtrate in the known manner.

The author has proved the practicability of this process by experiments with pure potassium platinochloride.

The process is applicable without any modification to the determination of ammonia and of nitrogen, if the latter can be converted quantitatively into ammonia. Platinum can also be determined in this manner after it has been separated out as a platinum double salt, or in combination with organic bases. In the organic platinum double salts the total chlorine and the platinum can be determined by this method in one portion.

The reduction of the platinum salts by formiates can also serve for the elimination of platinum in the separation of potassium and sodium. In this case we use ammonium formiate, which is produced in the solution by adding first a little formic acid and then ammonia, until the reaction is slightly alkaline.—*Zeit. für Analyt. Chemie*.

NOTE ON THE BROMINE HEAT-VALUE OF OILS AND FATS.

By J. A. WILSON.

IN a recent number of the *Analyst* (July, 1895, p. 146), Messrs. Hehner and Mitchell describe a new thermal method for the examination of oils and fats which, briefly described, is as follows:—

1 grm. of the sample is dissolved in 10 c.c. of chloroform in a vacuum-jacketted test-tube, 1 c.c. of bromine is added, and the rise of temperature noted. In default of a vacuum-jacketted test-tube, an ordinary test-tube packed in cotton-wool may be employed. The above observers find that the latter plan gives results two degrees lower than the use of a vacuum-jacketted test-tube; but this, of course, will depend on the total rise of temperature being greatest, say, with linseed oil, and lowest with oils such as cocoanut and palm-nut oils. I find, however, that up to a rise of 17° C. the observed rise of temperature + 1 gives very nearly the iodine value. I ought previously to have mentioned that Hehner and Mitchell find that the observed rise of temperature multiplied by the factor 5.5 gives very nearly the Hübl or iodine value.

I have made some determinations on oils and fats which sometimes come under my notice and, in the main, agree with the authors of the process as to accuracy and convenience. I find that in the case of cocoanut oil, which gives a very low thermal value, that the factor $\times 5.5$ gives at once almost the correct iodine value. With tallow, lard, and butter the observed rise of temperature

in a test-tube packed in cotton-wool requires the addition of 1 before being multiplied by the factor 5'5.

The following table corroborates the above remarks :—

Name of oil or fat.	Rise of temp. with bromine.	Calculated iodine value.	Observed iodine value.
Cocoanut oil	1'5	8'2	8'4
S. A. tallow	7'0	43'2	44'0
Olive oil (pure) ..	14'0	82'5	82'0
Rape oil	18'0	104'5	103'4

THE ANALYSIS OF TIN SLAG.

By HENRY BAILEY, F.C.S.

THE slag obtained in the smelting of tin ores, and which is technically known as "glass slag," to distinguish it from the particles of unburnt culm locally known as slag, consists principally of double silicate of alumina and iron, containing a variable amount of stannous silicate, minute shots of metal, and in rare cases unreduced stannic oxide, together with small quantities of lime, tungsten, &c.

For technical purposes a knowledge of the amounts of iron, tin, and silica present is usually required, and the following scheme has been devised for their rapid determination.

The principal difficulty experienced in the opening up of tin slag is to obtain the silica in a granular, easily filtered condition, at the same time obtaining all the tin in solution. The ordinary method of decomposing silicates by fusion with alkaline carbonates, with subsequent evaporation with hydrochloric acid, is inapplicable, owing to the volatility of tin chloride during the evaporation to complete dryness.

Two grms. of the slag, reduced to the finest possible state of division in an agate mortar, are placed in an evaporating dish with 10 c.c. red fuming nitric acid, and evaporated to complete dryness on a sand-bath, the heating being continued until brown fumes cease to be evolved.

The nitric acid decomposes the silicates, rendering the silica granular, at the same time converting all the tin present into insoluble oxide. Twenty c.c. of strong hydrochloric acid are then added, and boiled for some time: this can now be done, as, the tin being insoluble, there is no danger of loss as chloride.

When all soluble matter has dissolved, dilute with an equal bulk of water, and place two sticks of zinc—each about an inch long—in the solution, and allow to stand until the iron is all reduced to the ferrous state, and all action ceases. It is best to allow the assay to stand in a warm place for about an hour, to ensure complete reduction of the tin.

Remove the rods of zinc, carefully scraping off and washing back any adhering spongy tin; filter and wash: titrate the iron in the filtrate with standard bichromate of potassium. Wash the spongy tin and silica from the filter-paper back into the dish, add 10 c.c. strong hydrochloric acid and a few drops of nitric acid (just enough nitric acid to oxidise the tungsten), and warm until the silica appears white; dilute, filter, and wash the silica well with boiling water.

Through the warm filtrate pass a rapid current of sulphuretted hydrogen, and allow to stand in a warm place until the sulphide of tin has completely settled and the odour of SH_2 nearly dissipated; filter, wash, dry, carefully ignite, and weigh the stannic oxide. Wash the silica with dilute ammonia, and finally with water; dry, ignite, and weigh.

An approximate idea of the amount of tungsten present in the slag may be obtained by evaporating and igniting the ammoniacal washings from the silica in a weighed platinum dish, and weighing the residual tungstic acid.

When it is desired to determine the alumina present in

the slag, the solution containing the iron and alumina, instead of being titrated direct, is nearly neutralised with carbonate of soda, 10 grms. of sodic hyposulphite added, and boiled until the odour of SO_2 has disappeared. The mixed precipitates of oxide of alumina and sulphur are filtered off, washed, dried, ignited, and weighed. The filtrate, containing the iron, is acidified with an excess of hydrochloric acid, boiled until free from SO_2 , and titrated with standard bichromate.

ON THE CASTING OF STEEL.

By SERGIUS KERN, M.E. St. Petersburg.

At the Obouhoff Steel Works, St. Petersburg, great inconvenience was felt for a long time in casting large round ingots of 5 tons and upwards, for forging guns. The stream of steel falling from a considerable height into the mould, from the 30-ton ladles of the Siemens-Martin furnaces, gives rise to a considerable quantity of splashes, which in return produce cracks on the surface of the ingots.

The same annoyance was also observed in casting rectangular ingots of 25 to 30 tons for armour plates.

M. Posnikoff, the manager of the steel department of the above-named works, has devised a very simple method, preventing the steel from splashing. It may perhaps be already in use elsewhere, but anyhow it deserves mention.

A tube is prepared of thin sheet-iron, such as is used for roofing. The tube is 24 inches in inside diameter, and is suspended from an iron ring, to which there are rivetted three bars on the surface of the mould just before casting. The steel is poured from the bottom of the ladle into the middle of the iron tube. All the splashes are thrown on the walls of the tube, which gradually melts away during the rise of the surface of the liquid steel in the mould.

We had the pleasure of seeing this device in perfectly successful action at the Obouhoff Works, where it is now in constant use.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 81.)

CHAPTER VI.

ON THE CHARACTER IMPARTED TO FLAMES, AND TO AN ELECTRIC SPARK, DISCHARGE, AND ARC, BY THE SALTS OF CALCIUM.

The Luminous Spectra of Calcium.—I made some researches on the character imparted to flames, and to the electric spark, discharge, and arc, by the salts of calcium, for the purpose of finding out whether the luminous spectra of calcium, barium, and strontium had any common relation among themselves and with the luminous spectra of sodium, potassium, and lithium. I obtained some carbonate of calcium from several sources, to see if anhydrous calcic-oxide made from it was always the same, and whether this oxide could be brought to such a state of purity that, when volatilised in an oxyhydrogen blowpipe at the fusing-point of iridium, spectrum analysis would not show the sodium spectrum, assuming that the air does not supply any sodium.

For this purpose I used colourless and transparent Iceland spar, arragonite, white marble, prepared oxalate and sulphate, and carbonate which had been dissolved in water charged with carbonic acid.

In the preceding chapter I described the method of ob-

taining carbonate of calcium, of uniform composition, free from all foreign bodies except traces of sodium, and capable of being reduced, by means of a properly regulated temperature and a current of gas, to the form of pure oxide of calcium.

It is generally stated that anhydrous calcic-oxide is greyish; what I obtained was quite *white*, even after being kept for some time at the fusing-point of iridium. This oxide gives a *deep red* colour to that part of an oxyhydrogen flame whose temperature is high enough to melt platinum, and a *deep reddish brown* or chocolate-brown colour to the part which is nearly as hot as melting iridium. The colour is *sky-blue* at the temperature of melted iridium.

In my opinion, the *red flame tipped with yellow*, generally attributed to calcium, is due to the presence of sodium in the compounds experimented on. For the sodium line is visible in all calcium flames coloured *red with a yellow point*, and when the sodium line disappears the flame is coloured deep red, brownish red, or sky-blue, according to the temperature.

I did not see the sodium line in the luminous spectrum of calcium flames, when, just before making a spectrum analysis, I had taken the precaution of keeping the oxide of calcium for a sufficient length of time at the fusing-point of platinum, and when the carbonate used to make the oxide had been most carefully protected from *atmospheric dust*. The experiment gave no trouble, and the result was conclusive. It was always successful, provided that oxide of calcium *absolutely* free from *silica* was used; for this body, in the presence of oxide of calcium, retains sodium to such an extent that it is extremely difficult to eliminate it, even at the fusing-point of iridium.

So-called pure Iceland spar and arragonite contain from 1/7000th to 1/8000th of their weight of silica, and minute traces of sodium; nevertheless, when they are put on to the top of a cone of pure oxide of calcium on a sheet of platinum, and heated in an oxyhydrogen blowpipe, they colour the flame *red with a yellow point*, and show a very brilliant sodium spectrum. I have not carried the experiment through to the end, but, after my numerous failures, I am fully convinced that the sodium line will be visible until all the oxide of calcium derived from the spar or arragonite has been volatilised.

Oxide of calcium is more volatile than it is usually thought to be; it vaporises at the freezing-point of platinum, and at the fusing-point of iridium it is volatilised with such rapidity by an oxyhydrogen or oxy-coal-gas blowpipe, that the air becomes pungent for breathing.

The Spectrum of Calcium in an Oxyhydrogen Blowpipe.—Having described these facts, I will give the results of the spectrum analysis of a flame, as seen alternately by M. Rommelaere and myself, in the different conditions of our work.

Carbonate of calcium, looked upon as pure, but which had been for some time in contact with air, *under a bell-jar, the edge of which was ground, polished, and greased, and stood on a smooth sheet of glass*, was put into a conical cup on a recently heated sheet of platinum. I eliminated the carbonic acid and sodium absorbed from the air, by means of an oxyhydrogen blowpipe with an excess of hydrogen. This could be effectually done without volatilising much oxide of calcium.

Spectrum analysis of that part of the jet which impinged on the calcium salt showed at first a very strong sodium and a very weak calcium spectrum.

On passing the blowpipe jet over the surface of the calcium oxide,—renewed by means of a recently-heated platinum spatula,—the sodium spectrum decreases and the calcium spectrum increases in brightness. When the experiment is carefully done, all traces of the sodium line disappear before the appearance of the blue line in the spectrum of chlorine in hydrogen, at 135 micrometer divisions on the Bunsen spectroscop. *Having thus quite eliminated it, the oxide of calcium can be raised to the*

highest possible temperature, without causing the sodium line to reappear.

To make certain of the accuracy of this observation, I made experiments on every point. I heated the oxide of calcium in a conical cup, successively in oxyhydrogen with an excess of hydrogen, and with the exact proportion for the production of water, taking care each time to project on to the point of the oxide of calcium cone, resting on the sheet of pure iridium, that part of the flame where one obtains the maximum temperature—that of the fusing-point of iridium. *I was absolutely unable to cause the appearance of the sodium line.* Thus these observations left no doubt in my mind.

I found the spectrum of oxide of calcium to consist of bands and lines, or of ill-defined lines entirely, according to the temperature and the analyser used. The bands were only seen before the blue line appeared; after this blue line appeared, if the slit were sufficiently narrow, the bands became simplified,—they were better defined, and divided up into *ill-defined* lines.

The appearance of the bands did not seem to me to occur in the order of refrangibility. I first saw the second red band, then the nebulous green line, then the yellow and orange-yellow bands, and lastly the blue line.

Although they appeared in this order, when well above the fusing-point of platinum, yet, when using a sufficiently narrow slit, with hydrogen not brought to incandescence, the spectrum of pure oxide of calcium in an oxyhydrogen flame consists of a dark back-ground, marked by well-defined bands and lines, mentioned by M. Bunsen, in his "Spektral Analytische Untersuchungen," as occurring with chloride of calcium in a *hydrogen flame*.

The details of the calcium spectrum, both bands and broad lines, are so permanent that it is impossible to doubt that they are characteristic.

When I heated the *top* of a cone of pure oxide of calcium in an oxyhydrogen blowpipe, fed with two parts of hydrogen to one of oxygen, by volume,—which makes the *shortest* but *hottest* flame,—and took care to project the upper third of the inner cone of the blowpipe on to the oxide, the whole of the calcium spectrum became luminous, and a *pale violet-blue band* with hazy edges, situated between 148 and 149 micrometer divisions on my spectroscop (from 161.4 to 161.5 on that of M. Bunsen) appeared. This band appeared to consist of *at least two lines* very close together; it was very transient; at the slightest movement of the blowpipe, forward or backward, it became invisible. I was more successful in seeing the double blue line when subjecting to an oxy-coal-gas blowpipe some oxide of calcium formed by decomposing a cone made of a mixture of nitrate and oxide.* This oxide is very granular and is not displaced by the blowpipe flame so easily as anhydrous calcic oxide made from carbonate. The displacement of the latter oxide is inconvenient, because it admits of being easily reached by the blowpipe without being entirely volatilised. The incandescent solid then shows a continuous spectrum, which partially masks bands and lines of the calcium spectrum.

My observations of the double pale blue line in the flame spectrum of calcium date from the end of December, 1878. Having had occasion, during the summer of 1879, in collaboration with my late friend H. Sainte-Claire Deville, to melt *eighty-five grms.* of pure iridium in a lime crucible containing pure oxide of calcium, made by myself (an operation which is not difficult when metal containing a few thousandths of platinum is used, but

* To prepare a cone of granular oxide of calcium, I dissolved hydrate of calcium, without sodium, in a 10 per cent solution of nitric acid, distilled in platinum: after rapidly evaporating the solution down until it would solidify on cooling, I added enough hydrate of calcium, without sodium, to enable me to mould it into a cone. I immediately put this cone on a sheet of pure iridium, which had been previously heated to decompose the basic nitrate of calcium, and without delay I turned a coal-gas and air blowpipe on to it; and finally, I projected the inner cone of the shortest and hottest oxyhydrogen blowpipe flame on to the top of the cone.

which is extremely difficult with iridium entirely free from foreign bodies), we found, during the whole time we kept the metal melted in an oxy-coal-gas blowpipe, a *very strong* second blue line. Notwithstanding that there was an abundance of free oxide of calcium in the air throughout, we did not see the deep red calcium vapour; the gas inside the crucible was *sky-blue*. We saw exactly the same thing in an *oxyhydrogen blowpipe*. In addition to this, Messrs. H. Sainte-Claire Deville and Debray had, during their previous work, occasion to notice that the gas inside a lime crucible, when raised to the highest temperature attainable by a powerful blowpipe fed with oxygen and coal-gas, is coloured not *red*, but *blue*.

In order to see the double blue line, it is necessary to place the spectroscope as near as possible to the mouth of the furnace, taking care to arrange it obliquely, and especially outside the current of gas.

The Stability of the Combination of Sodium from the Air with Oxide of Calcium.—When left under a large bell-jar in air free from dust, oxide of calcium does not give the slightest indication of the presence of sodium; on heating it in air in an oxyhydrogen or oxy-coal-gas blowpipe, to a temperature at which the calcium spectrum is no longer visible, it colours the blowpipe flame pure yellow. Still, the sodium spectrum thus shown is very fugitive; it very soon disappears entirely with a sufficient rise of temperature, and reappears no more.

On the Flame Spectrum of Sulphate of Calcium.—Sulphate of calcium, made as described in the previous chapter, gave just the same spectrum as oxide of calcium in an oxyhydrogen or oxy-coal-gas blowpipe. This identity occurs throughout the time the sulphate is being fused, and persists after it is entirely dissociated, until enough oxide of calcium has been freed to render the remainder infusible. It is difficult to do this experiment in platinum, because the temperature of dissociation is the same as the fusing-point of platinum, this latter being attacked by the heated sulphate; but it succeeds beautifully when an oxyhydrogen or oxy-coal-gas blowpipe is projected on to a cone of spongy iridium on a concave sheet of platinum entirely covered with fused sulphate of calcium, or on to a cone of sulphate on a bed of pure iridium. When using the products of dissociation of sulphate, I saw the double blue calcium line, above mentioned, on a very bright back-ground; the products of dissociation were so evenly distributed that it was very easy to make observations.

(To be continued).

ON THE VOLUMETRIC DETERMINATION OF LEAD.

By ALLERTON S. CUSHMAN and
J. HAYES-CAMPBELL.

FRESENIUS, in the last edition of his "Quantitative Analysis," commenting on the volumetric determination of lead, says:—"Although there is no lack of proposed methods for the volumetric estimation of lead, we are still without a really good method for practical purposes, that is, a method which can be generally employed, and which is simple and exact."

Among the methods which have been proposed, one which has been so much used is that of Schwartz (*Dingl. Poly. Jour.*, clxix., 284), briefly outlined. This depends upon precipitating the lead as chromate in a sodium acetate solution with a standard solution of potassium bichromate, the end point being determined by an outside indicator consisting of drops of a neutral solution of silver nitrate on a porcelain plate. It is exceedingly difficult to decide when the first red tinge makes its appearance in the indicator, owing to the yellow colour of the precipitated lead chromate. The end point is therefore frequently overrun. W. Diehle (*Zeitschr. Anal. Chem.*,

1880, 306) modified the method by titrating the excess of bichromate in acid solution with sodium thiosulphate, the end point being indicated by the disappearance of the yellow colour of the bichromate. In our experience this modification does not lessen the difficulty of determining accurately the end point, owing to the fact that the yellow colour gradually shades off into a green in case a fair excess of bichromate has been added.

These considerations led us to endeavour to modify the original method in such a manner as to secure a simple and accurate means of determining the excess of bichromate present. This we accomplish by titrating the solution after filtering off the precipitated lead chromate, with a standardised solution of ammonio-ferrous sulphate, using potassium ferricyanide as an outside indicator, under exactly the same conditions observed in standardising bichromate solutions. The bichromate solution is made up of convenient empirical strength, and standardised against a weighed amount of pure dried ammonio-ferrous sulphate. Slightly more than the equivalent weight of the latter salt is then weighed out and dissolved in a litre of water, with the addition of a few drops of sulphuric acid. The solution is transferred to a stock bottle, into which is immediately poured a sufficient quantity of some light paraffin oil to form a layer over the solution, thus protecting it from oxidation. The stock bottle is fitted with a syphon tube and pinchcock, so that the solution can be drawn out when needed. With this arrangement change in strength of the ammonio-ferrous sulphate solution takes place very slowly, while, as a few moments only are required to titrate it against the standard bichromate, its exact strength can be easily determined from day to day.

In order to test this modification, we decided to try it against other technical methods recently proposed, as well as against a standard gravimetric analysis. A well-mixed sample of a crystallised galena, containing only a little silica as impurity, was first analysed by the method of Rose as given in Fresenius's "Quantitative Analysis." The lead is precipitated as the sulphide, with the proper precautions; the sulphide is then dried, ignited gently in a current of hydrogen, and weighed. The following results were obtained:—

No.	Weight taken. Grms.	Weight lead sulphide. Grms.	Lead sulphide. Per cent.	Lead. Per cent.
1	2'0000	1'9870	99'35	86'08
2	2'0000	1'9856	99'28	86'00
3	1'9988	1'9856	99'35	86'06

The next series of results were obtained by the method of Albert H. Low (*Journ. Anal. Appl. Chem.*, vi., 12). Briefly, the method consists in decomposing the ore with nitric and sulphuric acids, adding further an excess of sulphuric acid, dissolving the lead sulphate in a saturated solution of ammonium chloride, and precipitating metallic lead by means of strips of aluminum. The precipitated lead sponge is scraped off, pressed into a button, dried, and weighed. By this method the following results were obtained:—

No.	Weight taken. Grm.	Weight lead. Grm.	Lead. Per cent.
1	0'5000	0'4341	86'82
2	0'5013	0'4311	86'00
3	0'4972	0'4313	86'64
4	0'5025	0'4371	86'98
5	0'5019	0'4351	86'25
6	0'5223	0'4540	86'92

These figures show a general tendency to high results, which is accounted for by the difficulty of washing the lead sponge free from ammonium chloride. In view of the fact, however, that one of these assays can be made in about twenty-five minutes, the results might be considered fair enough for some technical purposes.

The next method tried was Knight's (*Journ. Anal. Appl. Chem.*, vi., 11) modification of Hempel's method. This consists essentially in the precipitation of the lead as oxalate, the decomposition of this salt by means of sulphuric acid and titration of the liberated oxalic acid, with potassium permanganate. This method did not yield concordant results in our hands, and the percentages found were invariably low. As the method did not present any advantage over others, either in points of accuracy or time, we discontinued work with it.

The modified Schwartz method we carry out as follows:—About 1 grm. of finely-pulverised ore is digested in a casserole or evaporating dish with 15 c.c. of a mixture of two parts nitric acid and one part sulphuric acid, until decomposition is complete. Ten c.c. more of sulphuric acid are now added, and the liquid evaporated until it fumes freely. Cool, dilute with 10 c.c. of dilute sulphuric acid (1—10), and then add gradually 40 c.c. of water. Heat to boiling, filter, and wash by decantation with dilute sulphuric acid (1—10), getting as little of the lead sulphate on the filter as possible. To the residue in the dish add 20 c.c. of strong ammonia, then make slightly acid with acetic acid. Boil until the lead sulphate is dissolved, then pour the liquid through the filter, having first moistened the paper with ammonia. Wash the filter with water containing ammonium acetate in solution, and finally once or twice with hot water. Cool the filtrate, and run in from a burette an excess of standard bichromate solution, stirring until the precipitate settles rapidly and the supernatant liquid has a yellow colour. Allow to settle for a few minutes, then filter, under pressure if possible; wash a few times, and titrate the filtrate against the standard ammonio-ferrous sulphate.

After a little practice the method can be carried out as above detailed in about thirty minutes. In case the ore is known to be free from bismuth and antimony, the method can be materially shortened. Instead of bringing the ore into solution with a mixture of nitric and sulphuric acids, nitric acid alone is used. After solution the acid is neutralised with an excess of ammonia, and then made acid with acetic acid: this dissolves any lead sulphate that has been formed. This solution is then immediately titrated with the bichromate and ammonio-ferrous sulphate solutions exactly as described above. The following table shows the agreement in the results obtained by this method:—

No.	Weight taken.	Calculated weight lead found.	Lead.
	Grm.	Grm.	Per cent.
1	0.9983	0.8570	85.84
2	0.9987	0.8578	85.82
3	0.9997	0.8588	86.08
4	0.9806	0.8421	85.88
5	0.9996	0.8570	85.72
5	0.9971	0.8558	85.84
7	0.9975	0.8580	86.02
8	0.9936	0.8533	85.90

In general it may be said that the results are a trifle low. The mean of the amount of lead recovered in twenty determinations carried out by one of us was 99.6 per cent of that taken.

We do not know that the modification as used by us has never before been tried, but our results appeared to possess sufficient value to warrant publication.—*Journ. Amer. Chem. Soc.*, xvii., p. 901.

Calculation of the Thermic Power of Coal according to Dulong's Rule.—G. Arth.—The author gives the analysis of seven varieties of coal, along with their calorific power as calculated and as determined by experiment. The greatest difference between the values is 1.85 per cent of the value determined.—*Bull. de la Soc. Chim. de Paris*.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting, January 23rd, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

PROFESSOR G. F. FITZGERALD, M.A., F.R.S., of Trinity College, Dublin, delivered the Helmholtz Memorial Lecture.

The position of the work of Helmholtz was considered with special reference to its chemical aspects, and the later work that had been grafted upon it. Some of the valuable points in the vortex atom hypothesis of matter were noticed, and some of its serious difficulties considered. Analogies on this hypothesis to the asymmetric carbon atom and to the benzene ring were pointed out. The applications of thermodynamics to chemistry were noticed, and a theoretically perfect semi-permeable diaphragm for non-volatile salts in solution, in which the actions at all points are known, was described. The theory that a substance in solution is like a substance in the gaseous state was criticised, and it was contended that from Helmholtz's work, and on dynamical grounds, the conditions could not be alike. The theory that there was combination between the solvent and body in solution was put forward as a complete explanation of the known phenomena of solution and electrolysis. It was pointed out how Helmholtz had, by his work, made important steps forward in several directions towards a dynamical explanation of Nature.

DISCUSSION.

The PRESIDENT said that there were two ways in which we may do honour to a great fellow worker who had passed away. The one is by a rehearsal of the great things he had done; the other—and perhaps this is rather that which the greatest would wish should happen after their own time has passed—is by a continuation of the lines of thought which they have started, and by following the work on which they have been engaged. Of the great variety of work which Helmholtz undertook—and there can scarcely be a greater scientific name than his, if the quality and variety of the work in which he engaged are taken into account—the lecturer this evening has naturally insisted on that side which Helmholtz himself selected as most appropriate when he was lecturing to this Society in the year 1881. These inquiries into the nature of molecules and other similar physical speculations which our lecturer this evening has touched upon, are of more recent growth. These are the problems which form our inheritance from that great man. Where work was so abundant there could scarcely be more than the enumeration of the great scientific results which we owe to Helmholtz. There are present this evening, besides many of our older members, several distinguished men of science who will say a few words on the subject of the lecture in proposing a vote of thanks to Professor Fitzgerald for the admirable exposition for which the Society is so much indebted to him.

Sir JOSEPH LISTER, P.R.S., said he had much pleasure in proposing a vote of thanks to Professor Fitzgerald for his profound and brilliant lecture. For his own part he felt himself in a world in which he was almost an entire stranger. These magnificent conceptions of physics must necessarily be nearly a *terra incognita* to the surgeon and physician. But physiologists and surgeons are deeply indebted to Helmholtz for what he did in their own domain. They recall with pride that Helmholtz was, in the first instance, a medical practitioner. It is an exceedingly remarkable fact in the case of such a profound and distinguished a physicist, that to the last he retained his love for his old subject, physiology. On this occasion it is not possible to allude to all that physiology owes to Helmholtz, but there are two questions to which reference might be made—his explanation of the accommodating

power of the eye for different distances, and what has been for physiologists and ophthalmic surgeons—although Professor Fitzgerald regarded it as a mere triviality in Helmholtz's achievements—the great invention of the ophthalmoscope, that beautiful instrument, by which the interior of the eye can be both illuminated and inspected. How much added to our knowledge of the physiology of the eye, and to the diagnosis of ophthalmic disease, and, consequently, to ophthalmic practice, and also to our knowledge of the various diseases which are found to be dependent upon or connected with affections of the eye—these discoveries, even if nothing else had been accomplished by Helmholtz, would be enough to secure the gratitude of physiologists and surgeons.

Dr. EDWARD FRANKLAND said he had great pleasure in seconding the vote of thanks. He expressed the feeling of every Fellow of this Society in saying that Professor Fitzgerald had given an hour's discourse of enormous interest and importance to chemists. It would take some time to study and analyse this discourse, and to adequately discuss it in detail; but, whilst chemists had listened to the discussion of numerous points of contact of the work of Helmholtz with their own department of science, they were led anew to admire the intellect of that great man who left, perhaps, no branch of human knowledge untouched during his career. Professor Fitzgerald's references to the application of vortex motions to the explanation of the chemical combination and valency were somewhat discouraging, and there were one or two other sections of his discourse which he hoped and believed were slightly too pessimistic. We may hope that when another four or five decades have passed we shall arrive at a point when these physical theories which appear to us at the present moment almost impossible of application to chemical science will then appear perfectly clear; and when in this room, possibly, another Helmholtz is to be honoured in this way, we shall have the satisfaction of seeing these beautiful physical theories applied with effect to those obscure chemical phenomena on which we are all so anxious to have more light thrown.

Lord RAYLEIGH said that he might be allowed to add his congratulations to the Society on having secured Professor Fitzgerald to give this most interesting lecture upon certain aspects of the work of Helmholtz. He has done it in a way that few others, indeed if any other, could do it. It is to be hoped that chemists will take into grave consideration the emphatic warning that Professor Fitzgerald has given, particularly as to the danger of supposing that there is any dynamical similarity between the condition of a gas and that of a dissolved substance in a liquid. He quite agreed with much that had fallen from Professor Fitzgerald upon that subject. There is possibly a risk of pushing formal analogies too far, and of supposing that there is a real dynamical similarity, whereas there is, perhaps, only a similarity in mathematical law. Many of the ideas that he has broached required prolonged thought and study to do justice to them. The new idea of the construction of a semi-permeable membrane composed of minute capillary apertures in a fluid of non-wettable material seems likely to throw great light upon a rather obscure subject. He had long been impressed with the idea that capillarity is very closely connected with many of the problems which we should like to understand better than we do, leading, perhaps, almost into the recesses of nature's chemical laboratory. His own familiarity with Helmholtz's work belonged to a different branch of the subject to that which Professor Fitzgerald had considered. Some thirty years ago he had studied with the ardour of youth Helmholtz's great work on the sensations of sound. Indeed, he had learned such German as he knew mainly from that book. It so happened that within the last year, in connection with work of his own, he had been revising and consolidating his knowledge of that work, and he was quite as much impressed as he ever was with the extraordinary force and ability with which all the difficult problems

that there arise are treated in turn by the distinguished author. Many of those who have written since upon the subject, and have criticised, perhaps too lightly, some of the positions assumed by Helmholtz—although, of course, no positions are to be considered as beyond criticism—seem to him not too be so familiar as they might be with the great work in which those positions were first of all set out. What Sir Joseph Lister and what Professor Frankland have said will be echoed by all who are acquainted with any side of Helmholtz's work, that everything that he touched was distinguished by his touch, and that there is scarcely any field of knowledge in which he has not, as it were, left his mark. All will agree that the object which the Society has had in view in commemorating the work of Helmholtz is a most excellent one, and that on this occasion it has been admirably attained.

Sir HENRY ROSCOE said that he could not say more than had been already said with regard to this lecture by Professor Fitzgerald, for which the Society was very grateful. He might add, perhaps, one personal reminiscence. He had the great honour and extreme pleasure, as President of the Society, of introducing Professor Helmholtz, in 1881, when he delivered the Faraday lecture here; and only a few months ago he happened to be at Heidelberg, and was speaking there to Professor Koenigsberger, the eminent mathematician, who was a very intimate scientific friend of Helmholtz. Koenigsberger spoke especially of Helmholtz's admiration, almost proceeding to reverence, for another great man who has passed away, who we are glad to reckon amongst the greatest of our countrymen, Clerk-Maxwell. Helmholtz used to talk of Clerk-Maxwell and his work as almost supernatural. Koenigsberger thought that Maxwell was in many respects superior as a scientific physicist to Helmholtz himself. This shows that Helmholtz, in his magnanimity and high character, was the last to belittle the work of others.

Professor ARMSTRONG said he would like to recall a fact to memory—that probably Helmholtz's Faraday lecture was the one Faraday lecture which was distinctly an original contribution, which we can be sure exercised a very important influence on the scientific world. A very large share of the attention which has been drawn to this subject of late years which van't Hoff, Arrhenius, and others have developed to such an extraordinary extent, has arisen out of that Faraday lecture by Helmholtz. Not only here but in Germany also it attracted very great attention, and was of very much consequence. To-night, again, the Society is to be congratulated very highly indeed that Professor Fitzgerald has most distinctly followed the example of the great man who gave the Faraday lecture in delivering a lecture of striking originality.

Professor POYNTING expressed his own gratitude and that of the other physicists present for the remarkable lecture to which they had had the privilege of listening.

The PRESIDENT said that there was one fact in respect to Helmholtz which had not been mentioned. Sir Henry Roscoe alluded to the fact of our own countryman, Clerk-Maxwell, having been ranked on the same plane as Helmholtz as a physicist. Helmholtz himself was half an Englishman. It is always said that in the making of great men the mother's share is a large one; and the mother of Helmholtz was an English woman. She was a Miss Penn, and was connected with the same family as the founder of Pennsylvania.

The vote of thanks on being put to the meeting was carried by acclamation.

Professor FITZGERALD, in replying to the vote of thanks, said that he regarded it is a very great honour to be asked to deliver this lecture, and felt very much flattered indeed by the way in which it had been received. He would feel fully compensated for any trouble it had cost him if it helped his fellow workers and honoured Helmholtz. To help others with information was not so high an aim as to help them with moral ideals. The former was his aim; the latter was provided for him by the sympathy

and encouragement of the Chemical Society. He thanked them for it.

PHYSICAL SOCIETY.

Annual General Meeting, February 14th, 1896.

Captain W. DE W. ABNEY, President, in the Chair.

THE CHAIRMAN, after referring to the position of the Society, called upon the Treasurer to read the balance sheet.

After a discussion on the financial status of the Society, in which a number of members took part, the ballot was held for the election of a President and Council for the ensuing year. The following gentlemen were declared duly elected:—

President—Capt. W. de W. Abney, R.E., C.B., D.C.L., F.R.S.

Vice-Presidents—Shelford Bidwell, M.A., LL.B., F.R.S.; Maj.-Gen. E. R. Festing, R.E., F.R.S.; Prof. J. Peiry, D.Sc., F.R.S.; G. Johnstone Stoney, M.A., F.R.S.

Secretaries—T. H. Blakesley, M.A., M.Inst.C.E., 3, Eliot Hill, Lewisham, S.E.; and H. M. Elder, M.A., 50, City Road, E.C.

Treasurer—Dr. E. Atkinson, Portesbury Hill, Camberley, Surrey.

Demonstrator—C. Vernon Boys, F.R.S.

Other Members of Council—Walter Baily, M.A.; C. V. Burton, D.Sc.; L. Fletcher, M.A., F.R.S.; R. T. Glazebrook, M.A., F.R.S.; Prof. A. Gray, M.A.; G. Griffith, M.A.; Prof. G. M. Minchin, M.A., F.R.S.; Prof. W. Ramsay, Ph.D., F.R.S.; Prof. S. P. Thompson, D.Sc., F.R.S.; and Prof. S. Young, D.Sc., F.R.S.

The CHAIRMAN read an obituary notice of the late Rt. Hon. T. H. Huxley.

A vote of thanks to the auditors was proposed by Prof. Carey Foster, seconded by Mr. Enright, and carried unanimously.

A vote of thanks to the officers was proposed by Prof. A. Gray, seconded by Mr. Rhodes, and carried unanimously.

A vote of thanks to the Chemical Society for the use of their rooms was proposed by the Chairman, and carried by acclamation.

The meeting was then resolved into an Ordinary Science Meeting, and

A paper "On the Determination of High Temperatures by the Meldometer," by Prof. RAMSAY and Mr. EUMORFOPOULOS, was read by the latter.

The meldometer, an instrument invented by Dr. Joly, of Dublin, consists essentially of a thin platinum strip, which can be heated by the passage of an electric current. Small fragments of a solid substance are placed on the platinum strip, and the temperature at which they melt is deduced from the length of the platinum strip, which has been previously calibrated by means of solids of known melting-point. The authors have used gold for the purpose of calibrating the strip, and have assumed Violle's value, 1045° C., for the melting-point of gold. A number of measurements have been made of the melting-points of the salts of sodium, lithium, strontium, barium, calcium, and lead. The results obtained, however, differ considerably from those of Heycock and Neville, and the authors have not been able to account for these differences.

Prof. RAMSAY said the chief advantage of the meldometer was that only a very minute fragment of the substance was required for the measurement, so that extreme purity of the sample could be secured. There was the disadvantage, however, that many substances undergo some change when heated in air. In reply to a question from Mr. Blakesley, Prof. Ramsay said that the property

of the platinum which was used to measure the temperature was its expansion.

Mr. CAMPBELL asked whether the zero of the instrument was found to be constant. In Cardew voltmeters it often took several hours for the needle to come back to zero after heating.

Mr. EUMORFOPOULOS, in reply, said that the zero was constant to within a quarter of a degree.

Prof. RAMSAY also exhibited a small direct-vision spectroscope, in which the eye-piece is moved in a plane perpendicular to the axis of the instrument by means of a micrometer screw. This form of spectroscope is found to be of great utility in verifying the position of lines in the spectrum.

NOTICES OF BOOKS.

Elementary Agricultural Chemistry and Zoology. By Sir CHARLES A. CAMERON, Professor of Chemistry and Hygiene, Royal College of Surgeons. Dublin: Hodges, Figgis, and Co. (Ltd.). London: Simpkin, Marshall, and Co. (Ltd.). 1896.

We have here a very compact and clearly-written work on chemistry and geology as they especially concern the farmer and the horticulturist,—in a word, the manufacturer of food. One of its great merits is that it explains the technical terms so freely—perhaps too freely—used by botanists and vegetable physiologists.

The author first gives an account of the chemical elements, atoms and their combinations, equivalents, molecules, atomicity, symbols, double decomposition, chemical formulæ, and nomenclature. He then proceeds to give a similar survey of the development of plants, the parts of the plant, protoplasm, the chemical composition of plants, their atmospheric food, and the nitrifying action of bacteria. The food of plants on the soil forms the subject of Chapter VIII.

The formation of soils is ably explained. The constituents of soils and their varieties are next described. The composition of a common soil is given as:—

Organic and volatile matters	..	8'60
Alumina		7'00
Ferric oxide		4'40
Lime		1'00
Magnesia		0'80
Potash		0'40
Phosphoric acid		0'22
Sulphuric acid		0'15
Chlorine		0'10
Silica and insoluble silicates	..	77'93

Concerning sandy soils we find a very suggestive hint:—"The soils on which the finest clarets in France are produced are incapable of yielding a wheat crop." It is admitted that worms, and even microscopic organisms, are powerful factors in producing fertility of soils."

Next follows the geological classification of the rocks, with remarks on the agricultural value of the soils, furnished by their comminution and decomposition. We are reminded of the facts that the millstone grit produces barren soils, and that those of the sandstones of the coal-measures are worthless,—for instance, the lands to the east and north east of Manchester. On the contrary, the Triassic rocks (keuper marls) form splendid meadows and orchards. The Lias formation yields fine pastures, on which the Stilton and other superior cheeses are produced. The chalk districts do not rank high from an agricultural point of view.

We find mention of the degradation of our climate since the tertiary period, and of the glacial epoch (or epochs?) which succeeded.

Chapters XIX., XX., and XXI. give a view of the

geology of England, Ireland, and Scotland. In discussing the improvements of soils the author gives a caution concerning liming, subsoiling, and irrigation, but recommends afforesting, which in Britain is almost rendered impossible by the law. If a useless region is planted it is at once heavily smitten by local taxation, a quarter of a century before the returns come in.

Sir C. Cameron has found that coprolites finely ground produced a better crop of turnips than an equal money's worth of superphosphates.

This book is not only useful in itself, but will enable an attentive reader to study larger works with advantage.

Chemistry for Engineers and Manufacturers. A Practical Text-Book. By BERTRAM BLOUNT, F.I.C., F.C.S., Consulting Chemist to the Crown Agents for the Colonies, and A. G. BLOXAM, F.I.C., F.C.S., Head of the Chemistry Department, Goldsmith's Institute, New Cross. Volume I.—Chemistry of Engineering, Building, and Metallurgy. Large 8vo., pp. 244. London: Charles Griffin and Co. (Ltd.), Exeter Street, Strand. 1896.

THIS work consists of two volumes, each of which it is announced will be sold separately. This is a judicious arrangement, since each of them appeals in a considerable degree to a distinct class of readers. Vol. I., now before us, is addressed to mechanical engineers, architects and builders, and to all engaged in the erection of plant and the production of power.

The first chapter treats of the chemistry of the chief materials of construction, classified as stones, bricks, cements, &c., structural metals, and roofing materials. Next follow useful instruction on the strength, permanence, and preservation of materials.

The chemistry of the sources of energy is considered in the second chapter. The author seems to forget that in hot and cloudless regions,—e.g., Australia,—the kinetic energy pouring from the sun can be utilised industrially without the drawback of coal-smoke and coal-miners. In the account of gaseous fuels we do not see that reference is made to the deleterious character of CO, which forms so important a constituent of coal-gas, and to its removal by the Crookes process. The applications of the electric furnace in metallurgy are scarcely appreciated as they merit. The direct transformation of heat into electric energy without the tedious and wasteful interposition of the steam-engine is not overlooked.

The chemistry of steam-raising forms the subject of Chapter III., and involves a careful consideration of hard waters, their behaviour in boilers, and the means for removing the objectionable saline matter,—in other words, for softening and purifying boiler-water. Anti-incrustating mixtures, it is recommended, should be sold under their own names and at their own market-prices.

Lubricants are discussed in Chapter IV. The very correct conclusion is drawn that every different kind of bearing needs a different lubricant to enable it to run with the least friction. Contrary to a common prejudice, olive-oil is not the best lubricant, as it readily becomes rancid,—i.e., acid. Mineral oils, used as lubricants, should have a flashing-point not below 150°, and in cylinder lubrication not below 200° to 250°. Fatty oils, it must be remembered, if diffused over fibrous and pulverulent substances, have the dangerous property of occasioning what is called "spontaneous combustion." One of the most dangerous substances, if thus moistened with a fatty oil, is weighted or loaded silk—a property of which fire-insurance companies should beware.

The second part of the volume treats of metallurgy. Metalliferous ores are classified into—

1. Such as occur native, pure, and alloyed, copper, bismuth, mercury, silver, gold, platinum and its group, though it must be remembered that copper and mercury are commonly found as true ores, i.e., in combination with non-metallic elements.

2. Oxides; iron, copper, tin, zinc, manganese, and aluminium.

3. Sulphides; lead, copper, zinc, antimony, and mercury. Iron occurs in vast quantities in combination with sulphur, but such ores as pyrites are generally used as sources not of iron, but of sulphur.

4. Carbonates; copper, zinc, lead, and iron.

5. Haloids, silver; aluminium and sodium.

6. Arsenides and antimonides; nickel and cobalt.

It is remarked that nickel is also found in quantity as a double silicate.

Platinum has latterly been found as an arsenide, PtAs₂, at Sudbury, in Canada. The mineral is known as sperry-lite.

To notice critically the processes indicated for winning each metal would far exceed the space at our disposal. We may say that the first part of this volume will be a valuable guide to persons engaged in designing chemical works and plant, whilst the second part is a key to more special metallurgical studies.

CORRESPONDENCE.

THE X RAYS.

To the Editor of the Chemical News.

SIR,—I notice in CHEMICAL NEWS, vol. lxxiii., p. 73, it is stated that a correspondent, whose name is not mentioned, has suggested the use of a vacuum tube consisting, not of glass, but of aluminium, for the production of Prof. Röntgen's X rays. I take the liberty of drawing your attention to the closing words of Mr. Swinton's article in *Nature*, Jan. 23, which show that Mr. Swinton had thought of using aluminium.

"Further, having regard to the great opacity of glass, it seems probable that where ordinary Crookes tubes are employed a large proportion of the active radiations must be absorbed by the glass of the tube itself. If this is so, by the employment of a tube partly constructed of aluminium, as used by Lenard, the necessary length of exposure could be reduced."—I am, &c.,

CLAYTON BEADLE.

February 16, 1895.

ESTIMATION OF INSOLUBLE PHOSPHATE.

To the Editor of the Chemical News.

SIR,—Mr. Edwards admits, in his letter to you on the above subject (CHEMICAL NEWS, vol. lxxiii., p. 72), that where there is any quantity of iron and alumina present in the material the volumetric uranium method of estimation of the insoluble phosphates, as proposed by himself, does not give reliable results. He goes on to say, however, that in ordinary cases the amount of oxide of iron and alumina is usually very small. With this statement I cannot agree; it is only in comparatively few cases that iron and alumina are not present in relatively large quantities in the "insoluble phosphate," as compared with the amount of phosphoric acid. The materials of which the average superphosphate are manufactured will rarely contain less than 2 per cent of oxide of iron and alumina. This, roughly speaking, would equal about 1 per cent on the manufactured article. Practically all of this would be found in the "insoluble." 1 per cent of oxide of iron and alumina would equal (taking half as iron and half as alumina), on calculation to normal phosphates, 2.15 per cent; or, in other words, about 50 per cent of the total insoluble phosphate usually present in superphosphates.

This is a factor, I take it, which we cannot afford to ignore when dealing with this uranium process.

I fully appreciate the advantages of a quick estimation of the "insoluble phosphate" in works, where the results

are so often required in a hurry as a guide to future operations, but would prefer to rely upon calculation to attain this result, rather than a process which I am afraid would be extremely liable to give very uncertain results.—I am &c.,

GEO. H. ALLIBON.

Messrs. Richardson Bros. and Co.'s
Manure Works, Belfast, February 18, 1896.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 4, January 27, 1896.

Utility in Human Pathology of Photographs taken by the X Rays.—MM. Lannelongue, Barthélemy, and Oudin.—Already inserted.

Nomination.—Prof. Rouché was elected a "free member" of the Academy, *vice* the late Baron Larrey.

Some Properties of the Rays of Röntgen.—Jean Perrin.—Already inserted.

Dark Light.—Gustave le Bon.—Already inserted.

Action of Heat on Mercurous Iodide.—Maurice François.—From the manner in which mercurous iodide behaves under the action of heat, the following results follow:—We cannot melt mercurous iodide without decomposing it. Mercury separates out at the bottom of the vessel. The supernatant mass is a mixture of mercurous and mercuric iodides. We can, without causing a decomposition, *i.e.*, without a separation of mercury, melt mixtures rich in mercuric iodide, such as the mixture of 2 mols. mercuric iodide and 1 mol. of mercurous iodide. Neither the melting-point nor the ebullition-point of mercurous iodide can be exact. We cannot, by simple fusion, obtain crystals of mercurous iodide free from mercuric iodide. Yet, as mercuric iodide has a lower solidification-point than mercurous iodide, the melted mixture of these two substances gives in the first place, whilst cooling, crystals of mercurous iodide. By removing the portion which remained liquid, I have found that we may obtain by fusion crystals of mercurous iodide containing interposed variable quantities of mercuric iodide.

Absorption of Light by Solutions of the Indophenols.—M. Bayrac and Ch. Canichel.—One of us has prepared a series of indophenols derived from ten different phenols. They are soluble in ether, alcohol, benzene, acetic acid, acetic ether, and ligroine. The colour of the solution differs with the solvent; the same solvent gives with the different indophenols solutions of the same colour. If we intercalate these solutions in the path of luminous rays which illuminate the slit of a spectroscope, we remark that they all give a spectrum formed of a red band very brilliant and narrow, and of a much broader band of low intensity composed of green, violet, and indigo. The region of the spectrum between these bands is absorbed, except for very shallow strata or exceptionally low concentrations. The authors have arrived at the following result:—If we dissolve weights of each substance proportional to the molecular weights in an equal volume of the same solvent, the red band occupies the same position in the different spectra obtained.

Compounds of anhydrous Aluminium Chloride with the Phenols and their Derivatives.—G. Perrier.—Not suitable for useful abstraction.

Russian Aniseed Oil.—G. Bouchardat and M. Tardy.—Russian aniseed oil consists chiefly of anethol. There are also present anisic camphor, called by Wallach *fenchene*, and anisic acetone, and a small proportion of anisic acid.

Production of Pure Gaseous Formic Aldehyd.—A. Brochet.—The author uses as his material trioxymethylene, which is dissociated by heat, yielding formic aldehyd free from carbon monoxide.

Bulletin de la Société Chimique de Paris.

Series 3, Vols. xiii.-xiv., No. 16 and 17, 1895.

Reduction of Nitric Oxide by Moist Iron or Zinc.—Paul Sabatier and J. B. Senderens.—From the experiments of the authors it appears that the nitric oxide is reduced, not merely to nitrous oxide, but to a considerable extent to free nitrogen.

Reduction of Nitrous Oxide by Metals in presence of Water.—Paul Sabatier and J. B. Senderens.—Nitrous oxide in solution is reduced to the state of nitrogen by magnesium, zinc, iron, and even cadmium, with the simultaneous formation of a little ammonia.

Volatilisation of Carbon.—Henri Moissan.

Reduction of Alumina by Charcoal.—Henri Moissan.

Study of the different Varieties of Graphite.—Henri Moissan.

Displacement of Carbon by Boron and Silicon in Melting Cast-iron.—Henri Moissan.

Study of the Graphites of Iron.—Henri Moissan.

Preparation of Sprouting Graphites in the Electric Furnace.—Henri Moissan.—The last six papers have been duly noticed under the *Comptes Rendus*.

Variations of the Rotatory Power in the β -Methyladipic Series.—P. Freundler.—This paper does not admit of useful abstraction.

Campholenic Derivatives. Campholenonitriles and Campholenamides.—A. Béhal.—This paper and that succeeding, by the same author, "On the Campholenic Acids and Campholenes," are not suitable for abstraction, and are scarcely of sufficient importance for insertion in full.

Non-existence of Stereoisomerism in the Amino-butenediolic Derivatives.—R. Thomas-Mamert.—The derivatives in question do not exhibit stereoisomerism.

Ethyl-aminobutenamidoates.—R. Thomas-Mamert.—Not suitable for abstraction.

New Preparation of Glycerose.—M. Fonzes-Diacon.—The author has obtained this aldehyd by dehydrogenating anhydrous glycerin with mercuric chloride.

Revue Universelle des Mines et de la Metallurgie.

Series 3, Vol. xxxii., No. 1.

On a New Procedure for the Extraction of Gold from Tailings, Slimes, and Concentrations.—B. de Wilde.—The author describes a modification of the cyanide process employed in the Transvaal, the United States, and New Zealand. His procedure consists of three operations—the solution of the gold, the recovery of the excess of cyanide, and the precipitation of the gold. He does not find that the addition of oxidising bodies to the solution of cyanide fails to produce any serious benefit. The mean consumption of cyanide is said to be 2 lbs. per ton of tailings; this quantity is capable of much reduction, probably down to $\frac{1}{2}$ lb. The excess of cyanide is recovered by adding to the liquid ferrous sulphate, until a few drops of the filtrate begin to give a blue colour on the addition of some drops of a solution of potassium ferricyanide. The gold remains in solution in the state of potassium auro-cyanide. The precipitation of the gold is based upon the following principle:—In a solution containing the double potassium auro-cyanide, we precipitate all the cyanogen as aurous cyanide, and cuprous cyanide on acidifying the solution by means of sulphurous acid, and then adding a solution of copper sulphate. The least excess of this salt effects the absolutely complete precipitation of the gold.

MISCELLANEOUS.

A Battle for a Word.—A controversy is at present raging in the pages of the *Chemiker Zeitung*. A certain firm lays claim to the exclusive right of applying the name "phenacetin" to one of its products,—a demand the more remarkable as the method of preparing this drug is not patented in Germany.

The Humus Theory in Agriculture.—In the *Chem. Zeitung* Dr. Gigli reviews a work by Prof. Adolfo Casali, on the part played by humus in the fertilisation of soils. The author shows that Saussure's humus theory contains a phase of truth which cannot be neglected, and that humus in fact contributes largely to the nutriment of plants, as it forms an excellent medium for microbial life.

Further Details on Argon and Helium.—Lord Rayleigh and Professor Ramsay have examined the gases given off from the hot springs of Bath, and find that they contain less argon than atmospheric air, but also helium. The gases from the Buxton springs contain about 2 per cent of argon, but the presence of helium is questionable. According to the latest results of the discoverer, argon is not a mixture, and cannot be an allotropic variety of nitrogen.

The X Rays.—A report is in circulation, though we cannot say on whose authority, that a Professor of the University of Perugia has rendered Prof. Röntgen's rays visible by means of a newly-invented instrument, which its author, Prof. Salvioni, names the iristoscope. G. d'Imperilla announces, in the *New York Electrical Engineer*, a process for secretly seeing and photographing objects at night or in darkness. A judicious reserve will be useful in speaking of any application of the X rays.

The Philadelphia Museums.—There are now established at Philadelphia a group of Museums, economic, educational, commercial, and scientific in their character and objects. Their purposes—those especially of the "Commercial Museum"—seem to be very similar in character to those of the Imperial Institute of London, as originally planned. It does not appear that any of them are intended to be perverted into places of amusement.

MEETINGS FOR THE WEEK.

- MONDAY, 24th.—Society of Arts, 8. (Cantor Lectures). "Chemistry of certain Metals and their Compounds used in Building, and the Changes produced in them by Air, Moisture, and Noxious Gases, &c.," by Prof. J. M. Thomson, F.R.S.E.
Medical, 8.30.
- TUESDAY, 25th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.
Society of Arts, 8. "The Palette of the Potter," by William Burton, F.C.S.
Medical and Chirurgical, 8.30.
Institute of Civil Engineers, 8.
Photographic, 8.
- WEDNESDAY, 26th.—Society of Arts, 8. "The Standard of Musical Pitch," by A. J. Hopkins.
British Astronomical, 5.
Geological, 8.
- THURSDAY, 27th.—Royal, 4.30.
Royal Institution, 3. "Some Aspects of Modern Botany," by Prof. H. Marshall Ward, F.R.S.
Society of Arts, 4.30. "The Tobacco Industry of India and the Far East," by C. Tripp.
Institute of Electrical Engineers, 8.
- FRIDAY, 28th.—Royal Institution, 9. "On Marine Organisms and their Conditions of Environment," by Dr. John Murray.
Physical, 5. Experiments with Incandescent Lamps, by Sir David Salomons. "On the Alternating Current Arc," by Messrs. Fleming and Petavel.
- SATURDAY, 29th.—Royal Institution, 3. "Light," by Lord Rayleigh, F.R.S., &c.

TO CORRESPONDENTS.

H. A. le Hill.—Communication received. Please forward address.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Quantitative Separation.—What is the best book to get on the quantitative separation of organic acids, alcohols, and ethers, such as are in fermented liquids of varying ages?—A. B.

Carbonic Acid.—Can any reader please answer me the following questions about carbonic acid? Assuming that when the gas is in the liquid state and in the presence of water or moisture it is capable of combining chemically to form the hydrate, in this state can it pass from the liquid to the gaseous without breaking up the combination? If so, would there be any action when the (hydrated) gas is passed over fused CaCl_2 or through conc. H_2SO_4 when under varying pressures?—F.C.S.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1892.

ON THE APPLICATION OF RÖNTGEN'S RAYS IN SURGICAL DIAGNOSIS.

By MM. LANNELONGUE and OUDIN.

It is necessary to ascertain to what degree the new rays can traverse the most compact parts of the human body, to show the state of the hard portions found there. To this end we have taken the thigh and the knee,—the first time, we believe, that the attempt has been made. The two subjects had tedious affections of this region of the body, and it was interesting to know if the diagnoses which had been carefully made beforehand would be confirmed by the new method of investigation.

The first subject is now cured of an osteo-arthritis of the left knee, of a tuberculous nature, which had required three years of successive treatment.

The second photograph which we present is that of the thigh of a child of 8 years of age, who had suffered from osteitis of the femoral diaphysis. He is now cured, and walks perfectly well.

The examination with the new light did not afford any novel information which had escaped notice, but it confirmed in all points the indications arrived at clinically.—*Comptes Rendus*, cxxii., p. 283.

INFLUENCE OF THE CHEMICAL NATURE OF SUBSTANCES, AND THEIR PERMEABILITY BY THE RÖNTGEN RAYS.

By MAURICE MESLANS.

NUMEROUS experiments have demonstrated that certain bodies are transparent to the radiations emitted by the Crookes tube, whilst others present as regards these rays a relative opacity. I have undertaken to examine what is the relation which may exist between the transparency of these substances and their chemical nature, and if the Röntgen rays may not furnish a new means of investigation in the domain of chemistry. I will here merely indicate the most striking of the results which I have obtained: they are manifest on an examination of the photographic proofs which I submit to the Academy, and which refer to about fifty substances, simple and compound. These results, though incomplete, seem to me to offer some very definite conclusions, and determine me to pursue this study further.

The transparency or opacity of bodies to the X rays is not absolute; the influence of thickness has been already demonstrated, and the rôle of density has been examined. The specific chemical nature appears to me to present a very considerable influence. I have compared together the various non-metallic bodies as well as their acid derivatives, and the salts, metallic or organic, which they yield. My experiments have related chiefly to organic bodies, and to their essential element, carbon.

I have been hitherto able to establish the extreme transparency not merely of carbon in its different states, compared to those of other non-metals, the slight opacity of organic compounds when along with carbon they contain merely the gaseous elements, hydrogen, oxygen, and nitrogen. Still this transparency is far from being uniform, and presents very various degrees which appear connected with the chemical function of these bodies.

The photographic proofs which accompany this me-

moir have been obtained by shutting up a photographic plate in a frame for negatives, and arranging upon the little board which covers the plate the substances whose transparency it was desired to study, lighting up the whole with a Crookes tube, placed at a distance of 20 c.m. After an exposure of thirty minutes, the plate and development gave silhouettes of the bodies experimented upon, the relative intensities of which measured their transparency.

Diamond, graphite, anthracite, sugar-charcoal, give a faint tinge of a tonality similar to that of wood or of paraffin of an equal thickness, whilst sulphur, selenium, phosphorus, iodine, afford very strong images of great opacity.

The organic substances, ethers, acids, nitrogenous substances, were easily traversed by the X rays, and gave images scarcely perceptible; but the introduction into the organic molecule of a mineral element, such as iodine, chlorine, fluorine, sulphur, phosphorus, &c., gives to the molecule a great opacity.

The sulphates of the alkaloids are in this case. In like manner iodoform is very opaque, whilst the alkaloids, picric acid, magenta, and urea are very opaque. Phthalyl fluoride is much more opaque than phthalic acid, although the molecular weights of the two bodies approximate very closely. The metallic salts possess a great opacity, but which varies with the metal and the acid.

These results are corroborated by the photography of hands and of small entire animals executed by Professor Röntgen and others. In these proofs the muscles remain transparent. They are, in fact, substances formed entirely of carbon, hydrogen, oxygen, and nitrogen. The bones, on the contrary, give strong images. The opacity is due to the mineral elements which they contain.

The differences in the chemical constitution of the matters forming nerves, blood, &c., will doubtless permit us to obtain their photographic images, thanks to their unequal transparency.

I hope to carry out with more exactitude these researches on definite chemical species, and I purpose studying the relation between the chemical constitution of bodies and their degree of transparency to the Röntgen rays. At present the result which seems established is the transparency of carbon and its compounds with hydrogen, oxygen, and nitrogen, and the great opacity occasioned by the introduction into the organic molecule of other mineral elements, especially Cl, S, P, and above all I.—*Comptes Rendus*, cxxii., p. 309.

APPLICATION OF RÖNTGEN'S METHOD.

By ALBERT LONDE.

I HAVE the honour of submitting to the Academy a photograph obtained by Röntgen's method. This proof represents the pinion of a pheasant killed by shooting. The fracture of the bone is perfectly visible; we distinguish a detached fragment of bone, and a shot which has been embedded in the flesh.

I wish to point out the perfect transparency for the X rays of the photographic image as it is generally obtained. The heavy shades which in the ordinary processes do not allow the light to traverse, save in a rudimentary manner, appear as transparent to the X rays as to the large light parts. To verify this fact we have operated on films of celluloid, which does not arrest the X rays like glass.

On the other hand, we have exposed plates of different sensibilities, during equal times and at equal distances. We have decided that the impression was much more energetic on the rapid plates, and that the strength of the image was directly in proportion to the sensitiveness of the preparation.

The photographic plates therefore behave with the X rays exactly as with light.—*Comptes Rendus*, cxxii., p. 311.

ON A
MECHANICAL ACTION EMANATING FROM
THE CROOKES TUBE ANALOGOUS
TO THE PHOTOGRAPHIC ACTION DISCOVERED
BY RÖNTGEN.

By MM. GOSSART and CHEVALIER.

WE have the honour of pointing out to the Academy a field of mechanical force manifested in the interior of the Crookes radiometer when fixed opposite to a Crookes tube.

We wished, in a course of public lectures on the radiations of electric lamps, to introduce Röntgen's X rays, the cathodic rays of Crookes, and the stratified light of Abria, which led Crookes to his discovery by the augmentation of the strata. It seemed to us logical to manifest at a distance the heating of the Crookes tubes by means of his radiometer. Our surprise was great on seeing the vanes of the radiometer not merely remain motionless before a very hot tube, but, even if once set in motion by means of extraneous heat, stop in front of the tube with a very fixed orientation, and after pendulum oscillations which are the more rapid as their distance from the tube decreases.

It is clear that we were confronted with a mechanical action due to a field of force erected in the radiometer, and antagonistic to that of heat.

We fell to work to verify the existence of this field of force around the Crookes tube, by studying it with the radiometer as to direction and intensity, and proving, upon some twenty substances, that this force traverses the same media, or is arrested by the same substances, as the X rays.

Furthermore, when once the radiometer is placed in the Crookes field, and only then, we found that the field, viscous in some degree, which stops the vanes, is modified by currents, especially by that of the exciting coil of the Crookes tube, modified by substances, electrified statically, and is lastly disturbed energetically by a magnet. On moving a magnet around the sides of the radiometer, we as it were unscrew the vanes, and render them anew obedient to the source of heat.

Thus we may cause, simultaneously or successively, the X rays, heat, and electrostatic, electro-dynamic, and magnetic forces, to enter into action upon the vanes of the radiometer.

It seems to us, therefore, that we have a convenient instrument with qualitative and quantitative indications for making new investigations on the radiations, still mysterious, which emanate from the Crookes tube,—an emission following the exciting sources, the transmission, &c.

We therefore set up on a Melloni stand:—1. A Locatelli lamp. 2. The radiometer at 30 c.m. from the lamp, so as to give about fifteen rotations per minute. 3. The Crookes tube, movable on its right axis by means of an index which shows, on a graduated circle, the various directions of the axis of the cathodic sheaf of rays.

As soon as we project the cathodic rays there is an arrest of the vanes, and not in consequence of a dissymmetry of the system, since we have seen sometimes the one and sometimes the others take the axial direction of equilibrium. Unfortunately we have not yet been able to procure an apparatus with the vanes.

If we extinguish the Crookes tube, the stoppage persists for about five minutes in spite of the constant action of the Locatelli lamp. A fantastical and perhaps suggestive means of setting them again in motion is to project anodic rays, bringing the tube of the radiometer within a few millimetres. The vanes undergo at first an impulse in the direction opposite to the normal movement, which they afterwards resume.

We have determined a first line of the level of the field by actuating our single Crookes tube with a large Ruhmkorff's

coil and a primary current of 20 volts. This line is determined by the cessation of the stoppage; it is normal to the direction of one of the pairs of vanes; its maximum distance from the tube was 3 c.m. in front of the axis (distance from side to side), and it coincided with the tube towards the centre of the concave cathode.

On enclosing the tube with a circular photographic film, shut up in a paper case lined with metal letters, we were able to verify approximatively the concordance of the two fields.

Relatively to the sources, we can only make definitely this remark: the inertia of five minutes in the stoppage, which is manifested with a Ruhmkorff coil, is not obtained with a Wimshurst machine.

Our experiments were particularly directed to the transparency of the substances for the force of the photographic action. The following substances were very pervious for both radiations:—Pasteboard, ebonite, felt (layer of 2 c.m.), sulphur, paraffin (1 c.m.), wadding, &c. With equal thickness the action is propagated further through paraffin than through air.

As opaque bodies we indicate, in the order of decreasing opacity,—Lead, copper, aluminium, ivory, retort-coke.

This note may be the point of departure of a series of researches which we hope to pursue to study the field of the Crookes tube with the radiometer.—*Comptes Rendus*, cxxii., p. 316.

INCREASE OF THE PHOTOGRAPHIC YIELD
OF THE RÖNTGEN RAYS BY MEANS
OF PHOSPHORESCENT ZINC SULPHIDE.

By CHARLES HENRY.

IF we apply on the surface of a photographic plate opposite to the gelatino-bromide a layer of my phosphorescent zinc sulphide, of from 0.5 to 1 m.m. in thickness, having care to reserve half the plate taken longitudinally, and if we expose in a frame provided with a curtain successive bands of this plate to the light of a candle for increasing times, we naturally obtain, after developing and fixing, a series of tints of decreasing intensities, but we find between the two halves of the plate (that which has received zinc sulphide on the glass, and that which has not received it) a notable difference in the intensity of the grey tones; we see, e.g., on one of the proofs thus obtained, that the blackest half-band of those behind which there is no zinc sulphide has the same intensity as a half-band coated beneath with zinc sulphide, but exposed for only one-seventh of the time.

The ultra-violet rays pass, therefore, through the gelatino-bromide and the glass, and act upon the zinc sulphide, and the sulphide continues the reductive action by its own radiations, even on plates not sensitised to a yellowish green, then by its most refrangible radiations and by others, as will be seen at the end of this paper.

The Röntgen rays often behave quite differently in these conditions; if we expose to this radiation with the ordinary arrangement a gelatino-bromide plate sulphuretted in certain regions on the side opposite to the sensitive surface, we find on some plates no difference between the intensities of the parts the opposite side of which has been sulphuretted, and the intensities of those when the opposite side has been left untouched.

As the zinc sulphide is very easily saturated with the light of the Röntgen radiation, and as in certain cases this sulphide is acted on through the glass and the gelatino-bromide, we must conclude that, in the plates in question it is not the gelatino-bromide but the glass which plays the part of absorbent. This is a new demonstration of the difference between the Röntgen rays and the ultra-violet rays, and the importance which must be ascribed to the glass and to its thickness in the cases where we

wish to sensitise the plates to these rays by the application of zinc sulphide to the opposite side of the plate.

If we photograph by the ordinary procedures, by daylight, an image painted with phosphorescent zinc sulphide, the parts to which the greatest thicknesses of the sulphide have been applied appear on the negative in white, more or less intense. On examining the behaviour of an object covered with phosphorescent zinc sulphide as regards the Röntgen rays, I have observed the remarkable fact of a striking increase of the photographic efficacy of the rays.

In a first experiment I photographed two fingers, the fore and the middle finger, the fore-finger having been coated with sulphuretted vaseline. It was found that all that portion of the plate which surrounds the shadow is blacker than the rest.

In a second experiment I placed on the photographic plate, wrapped in needle paper, an iron wire, and on this iron wire, in succession from the left to the right, a piece of 0.05 frc. intact, a piece of 0.10 frc. coated with sulphide on its anterior surface, a piece of 0.10 frc. coated with sulphide on its anterior surface, a piece of 0.05 frc. coated with sulphide on its posterior surface, a 5-frc. piece in silver coated with sulphide on the larger part of its anterior surface; lastly, a small optical trough, cylindrical, divided into two compartments, and containing in the right-hand compartment a solution of quinine sulphate. The plate being developed and fixed after an exposure of forty-five minutes gives a very distinct shade of the iron wire behind the coin of 0.10 frc. coated with sulphide on its anterior surface, a shade rather less definite behind the portion of the coin of 0.05 frc. coated with sulphide on its posterior surface (the shadow of this piece coming up lighter than the others), a shadow less distinct also behind the portion of the 5-frc. piece coated with sulphide (silver being under equal conditions more transparent than bronze); on the other hand, there appeared no shadow of the wire behind the sou left intact, and behind the portion of the 5-frc. piece not coated with sulphide. Quinine sulphate did not exert any appreciable effect.

This experiment proves that it is possible, by coating with phosphorescent zinc sulphide bodies capable of absorbing Röntgen's rays, to render visible on the photographic plate objects situate behind such bodies and otherwise invisible. The zinc sulphide fulfils the office of a supplementary actinic source; it converts into photographic rays Röntgen's rays which are inert in this respect, a new proof of the complexity of the radiations emitted by the Crookes' phial.

It is probable that other sulphides besides the phosphorescent zinc sulphide possess this property. I have not had the leisure to try them; but the great inalterability of the phosphorescent zinc sulphide secures for it an incontestable superiority over all other artificial phosphori.

I have likewise had occasion to verify, in the phosphorescent zinc sulphide, a hypothesis of Henri Poincaré. "May we not then ask ourselves if all bodies whose phosphorescence is sufficiently intense do not emit in addition to luminous rays the X rays of Röntgen, whatever may be the cause of their fluorescence?"

I have exposed for a second to the light of a magnesium ribbon a parallelepipedal ingot of aluminium, 0.145 metre long, 0.145 metre broad, and 0.006 metre thick, resting on a small support of blackened cardboard. On the outside for a length of 0.06 metre, I coated it with zinc sulphide; then I left intact, externally and internally, a surface of 0.05 in length; lastly, I coated the ingot with this same sulphide internally on a surface of 0.038 in length, almost entirely shaded from the light of the magnesium, except at the edges. I placed between the ingot and the photographic plate, covered with a double sheet of needle paper, the above-mentioned iron wire. After developing and fixing the negative presented a slight white silhouette of the wire on the rectangular black ground of the shadow of the ingot. The difference of

tints imperceptible in the non-sulphuretted portion of the aluminium plate is more appreciable in the portion of the plate corresponding to the portion of the plate sulphurised below. In the same manner, after exposing the ingot to diffused daylight from three to five hours on a plate covered with a double sheet of needle paper, I obtained a very distinct veil of the plates visible, as far as the confines of the part sulphuretted internally. — *Comptes Rendus*, cxxii., p. 312.

PHOTOGRAPHIC PROOFS OBTAINED BY MEANS OF THE X RAYS.

By CH. V. ZENGER.

THE interposition of a plate of wood of several m.m. in thickness prolongs the time of exposure and injures the distinctness of the images by the penumbra which is formed. The defects of the homogeneity of the wood produce streaks in the silhouettes, whilst the use of proofs for surgical diagnosis would require a great precision in the details. I have dispensed with the plate of wood, and I have placed the hand directly on the gelatino-bromide plate, interposing merely a black paper very homogeneous. The image is as definite as possible, and the time of exposure may be reduced to less than an hour.

I have the honour of submitting to the Academy the three following silhouettes:—

1. The hand of my assistant applied on the sensitive plate without anything intervening. The proof shows the bones, the motor muscles, and a gold ring. Time of exposure 45 minutes.

2. A hand into which four fragments of glass had penetrated in the thumb; three of the fragments had been previously extracted, but the fourth is still fixed in the thumb.

3. A hand affected with Morvan's disease. The first joints have already been amputated. We distinguish the progressive destruction of the bones, the parts attacked presenting a greater transparency. Exposure 90 minutes.

I am convinced that the best means of attaining the utmost possible distinctness is to place the sensitive plate in direct contact with the object, and to make use of high tensions so that the Crookes tube may be placed as far as possible without too much prolonging the time of exposure.—*Comptes Rendus*, cxxii., p. 315.

THE PAST, PRESENT, AND FUTURE WATER SUPPLY OF LONDON.*

By E. FRANKLAND, D.C.L., LL.D., F.R.S.

IN a discourse to the members of the Royal Institution on the subject of the Metropolitan water supply nearly thirty years ago, I stated that out of every thousand people existing upon this planet three lived in London; and, as the population of London has in the meantime doubtless grown at a more rapid rate than that of the rest of the world, it will probably be no exaggeration to say that now, out of every thousand people alive on this earth, four live in London; and, therefore, any matter which immediately concerns the health and comfort of this vast mass of humanity may well merit our most earnest attention. Amongst such matters, that of the supply, in sufficient quantity, of palatable and wholesome water is certainly not the least in importance.

It is not, therefore, surprising that this subject has received much attention from several Royal Commissions,

* Condensed report of a Lecture delivered at the Royal Institution, Friday, February 21, 1896.

notably from the Royal Commission on Water Supply of 1867, presided over by the Duke of Richmond; the Royal Commission on River Pollution and Domestic Water Supply of Great Britain, presided over by the late Sir William Denison, of which I had the honour to be a member; and, lastly, that of 1892, of which Lord Balfour of Burleigh was the Chairman.

The Royal Institution has, for nearly three-quarters of a century, been prominently connected with the investigation and improvement of the Metropolitan water supply; no less than four of our Professors of Chemistry have been successively engaged in this work, namely, Professors Brand, Odling, Dewar, and myself; whilst three of them have been members of the Royal Commissions just mentioned. I may, therefore, perhaps be excused for bringing the subject under your notice again for the third time.

On the present occasion, I propose to consider the subject from three points of view, viz., the past, the present, and the future; and, for reasons which will appear hereafter, I shall divide the past from the present at or about the year 1883, and will not go back further than the year 1828, when Dr. Brand, Professor of Chemistry in the Royal Institution, Mr. Telford, the celebrated engineer, and Dr. Roget, Secretary of the Royal Society, were appointed a Royal Commission to enquire into the quality and salubrity of the water supplied to the Metropolis.

The Commissioners made careful examinations and analyses, and reported as follows:—"We are of opinion that the present state of the supply of water to the Metropolis is susceptible of, and requires, improvement; that many of the complaints respecting the quality of the water are well founded; and that it ought to be derived from other sources than those now resorted to, and guarded by such restrictions as shall at all times ensure its cleanliness and purity. (At this time the water was pumped from the Thames between London Bridge and Battersea). To obtain an effective supply of clear water free from insects and all suspended matter, we have taken into consideration various plans of filtering the river water through beds of sand and other materials; and considering this, on many accounts, as a very important object, we are glad to find that it is perfectly possible to filter the whole supply, and this within such limits in point of expense as that no serious objection can be urged against the plan on that score, and with such rapidity as not to interfere with the regularity of the service."

Before the year 1829, therefore, the river water supplied to London was not filtered at all; but after the issue of this report, the companies set themselves earnestly to work to improve the quality of the water by filtration.

In the year 1832, and again in 1849, London was severely visited by epidemic cholera, and the agency of drinking-water in spreading the disease forced itself upon the attention of the observant portion of the medical profession. It was Dr. Snowe, however, who, in August, 1849, first formally enunciated the doctrine that drinking-water polluted by choleraic matters is the chief mode by which cholera is propagated.

In every visitation of Asiatic cholera to London, the water supply was either altogether unfiltered or imperfectly filtered, besides being derived from highly polluted parts of the Thames and Lea; and the enormous loss of life, amounting in the aggregate to nearly thirty-six thousand people, can only be attributed to this cause; for it has now been satisfactorily proved that cholera is, practically, propagated by drinking-water alone; and that efficient filtration is a perfect safeguard against its propagation. Moreover, it is most satisfactory to know that, since the year 1854, no case of Asiatic cholera in London has been traced to the use of filtered river water. The first effect of Dr. Snowe's cardinal discovery was the removal of the intakes of the river water companies to positions beyond the reach of the tide and of the drainage of London. The second was the greater attention paid to the efficiency of filtration.

Such is the verdict with regard to cholera, and the same is true of the other water-borne disease—typhoid fever. But, unlike cholera, this disease is disseminated in several other ways, and its presence or absence in any locality may not of necessity have any connection with drinking-water, as is strikingly shown by the health statistics of Manchester; since the water supply of Manchester, derived as it is from mountain sources, is above all suspicion of this kind. These other causes have, during the last ten years, been much mitigated in London by various sanitary improvements, whilst, as shown in the diagram on the screen, there has been no corresponding mitigation in Manchester. There is no evidence whatever that since the year 1869, when typhoid fever appeared for the first time as a separate disease in the Registrar General's reports, it has been conveyed by the water supply of the Metropolis.

Although very soon after the year 1856 all the water supplied to London was obtained from sources much less exposed to drainage pollution, it was still very carelessly filtered. Previous to the year 1868, there are no records of the efficiency, or otherwise, of the filtration of the Metropolitan water supply derived from rivers; but at that time I began to examine these waters for turbidity. In that year, out of 84 samples, 7 were very turbid, 8 turbid, and 10 slightly turbid; so that, altogether no less than nearly 30 per cent of the samples were those of inefficiently filtered water. The Metropolitan water supply then, up to the year 1868, may be shortly described as derived for many years from very impure sources with either no filtration at all, or with very imperfect filtration; and afterwards, when the impure sources were abandoned, the supply was still often delivered in a very inefficiently filtered condition. But after the establishment of monthly reports, the quality of these waters gradually improved in this most important respect down to the year 1883, since which time the efficiency of filtration of all the river waters supplied to the Metropolis has left little to be desired.

What is it then that separates the past from the present water supply of London? In the first place there is the change of source—I mean the change of the position of the intakes of the several companies drawing from the Thames and Lea, and the total abandonment of the much-polluted Ravensbourne by the Kent Water Company. So long as the water was derived from the tidal reaches of the Thames and Lea, receiving the drainage of an immense population, the risk of infection from water-borne pathogenic organisms could scarcely be otherwise than imminent; for, although we now know efficient filtration to be a perfect safeguard, anything short of efficiency must be attended with risk in the presence of such extreme pollution.

Nevertheless, the line of demarcation between the past and the present water supply of the Metropolis is, in my opinion, to be drawn, not when the intake of the river companies were removed to positions beyond the possibility of pollution by the drainage of London, but it must be drawn at the time when efficient filtration was finally secured and ever since maintained; that is to say, in the year 1884.

The removal of turbidity by sand filtration, however, refers only to suspended matter, but there are sometimes objectionable substances in solution, of which organic matter is the most important. River water and mountain water, even when efficiently filtered, contains more organic matter than spring or deep-well water; but this is reduced in quantity by storage and especially by filtration, although it can perhaps never be brought up to the standard of organic purity of spring and deep well water.

The Present Water Supply.

At present London is supplied with water from four sources—the Thames, the Lea, the New River, and deep wells. Of these, the deep wells yield, as a rule, the purest water, requiring no filtration or treatment of any

kind before delivery for domestic use. The river waters, on the other hand, require some kind of treatment before delivery; storage and subsidence in reservoirs, and filtration. The water from the Thames is abstracted at and beyond Hampton; that from the Lea is taken out at two points, viz., at Angel Road, near Chingford, by the East London Water Company, and above Hertford by the New River Company, who convey it to Green Lanes by an open conduit 25 miles long called the New River Cut, in which it is mixed with a considerable volume of spring and deep well water.

Hitherto I have spoken of chemical purity, or comparative freedom from organic matter, only. But the spread of diseases, such as cholera and typhoid fever, through the agency of drinking-water has no connection whatever with the chemical or organic purity of the water. These diseases are propagated by living organisms of extreme minuteness, to which the names bacilli, bacteria, microbes, and others have been given; and here comes the important question—How does filtration secure immunity from these water-borne diseases?

To Dr. Koch, of Berlin, we are indebted for the answer to this question. By his discovery of a means of isolating and counting the number of microbes and their spores in a given volume of water we were, for the first time, put into possession of a method by which the condition of water as regards these living organisms, before and after filtration, could be determined with quantitative exactness. The enormous importance of this invention, which was first made known and practised in England in 1882 by the late Dr. Angus Smith, is evident when it is borne in mind that the living organisms, harmful or harmless, contained in water are of such extreme minuteness as practically to defy detection by ordinary microscopical examination. But, although the microscope cannot detect with certainty single bacteria or their spores, even the naked eye can easily discern towns or colonies consisting of thousands or even millions of such inhabitants.

Dr. Koch's method accomplishes at once two things—it isolates, in the first place, each individual microbe or germ; and, secondly, places it in conditions favourable for its multiplication, which takes place with such amazing rapidity that even in a few hours, or at most in two or three days, each organism will have created around itself a visible colony of innumerable members—a town, in fact, comparable to London itself for population. By operating upon a known volume of water, such as a cubic centimetre, for instance, the number of separate organisms or their spores in a given volume of the water under investigation can thus be determined.

In order to ascertain the effect of filtration upon the bacterial quality of the water, it is absolutely necessary that the sample should be taken immediately after it has passed through the sand filters; for if it be obtained from the delivery mains in town—that is to say, after the water has passed through many miles of pipes—the rapid multiplication of these organisms, except in very cold weather, is such that a water which contains only a single living organism per c.c. as it issues from the filter, may contain 100 or 1000 in the same volume when, after several hours, it arrives at the consumer's premises.

Now, what is the effect of sand filtration as carried out by the various water companies supplying London upon the living matter contained in the raw river water? It is simply astounding. Water which is poured upon sand filters containing thousands of bacteria per c.c.—for a single drop of Thames water sometimes contains 3000 separate living organisms—comes out from those filters with 50, 30, 10, or even less of these organisms per c.c., or the number of microbes in a single drop is reduced to 2, or even none.

Rather less than one-tenth of the total volume of water supplied to London is derived by the Kent Water Company from deep wells in the chalk. As it issues from the porous rock into the fissures and headings of these

wells, this water is, in all probability, absolutely sterile; but by the time it has been pumped up to the surface, it usually contains a small number of microbes. Thus, during the year 1892 it contained, on the average, 6 per c.c.; in 1893, 13; in 1894, 15; and in 1895, 8.

Thus, although the deep well water has, from a bacterial point of view, a decided advantage, the filtered river waters are not very far behind, and there is every reason to believe that, with the improvements that are now being carried out by the various river water companies, the Kent Company's water will before long, be run very hard by the other supplies.

By the examination of the water as it issues from the filters, the utmost freedom from microbes, or maximum degree of sterility, of each sample is determined. This utmost freedom from bacterial life, after all sources of contamination have been passed, is obviously the most important moment in the history of the water, for the smaller the number of microbes found in a given volume at that moment, the less is the probability of pathogenic organisms being present; and, although the non-pathogenic organisms may afterwards multiply indefinitely, this is of no consequence in the primary absence of the pathogenic. But it is only fair in describing the character of the present water supply of London to say that not a single pathogenic organism has ever been discovered, even in the unfiltered water as it enters the intakes of the various companies, although these organisms have been diligently sought for. It is sometimes even said that the non-pathogenic organisms found in water may be beneficial to man, but this idea is not borne out by their entire absence from the food which Nature provides for young animals; milk is absolutely sterile, if healthy.

As it is at present impracticable to obtain water, uniformly at least, free from microbes, it is desirable to adopt some standard of bacterial purity, and 100 microbes per c.c. has been fixed upon, by Dr. Koch and myself, as the maximum number allowable in potable water. This standard is very rarely infringed by the London water companies, whilst I have every reason to hope that in the near future, now that special attention is directed to bacterial filtration, it will not be approached within 50 per cent. This hope is based, not only upon my own observations, but also upon the exhaustive and important investigations carried out at the Lawrence Experiment Station by the State Board of Health of Massachusetts under the direction of Mr. George W. Fuller, the Official Biologist to the Board. More than six years have already been spent in the prosecution of these American experiments, and many thousands of samples of water have been submitted to bacterial cultivation.

These important experiments, and my own observations on the London waters continued for four years, lead to the following conclusions:—

1. The rate of filtration between half a million and three million gallons per acre per day exercises practically no effect on the bacterial purity of the filtered water. It is worthy of note that the rates of filtration practised by the several water companies drawing their supplies from the Thames and Lea are as follows:—Chelsea Company, 1,830,000; West Middlesex, 1,359,072; Southwark Company, 1,568,160; Grand Junction Company, 1,986,336; Lambeth Company, 1,477,688; New River, 1,881,792; and East London, 1,393,920. Hence, not one of the London companies filters at the rate of two million gallons per acre per day; at which rate, in the Massachusetts filters, 99.9 per cent of the microbes present in the raw water were removed.

2. The effect of the size of sand grains used in the filters is very considerable. Thus, by the use of a finer sand than that employed by the Chelsea Company, the West Middlesex Company is able, with much less storage, to attain an equal degree of bacterial efficiency.

3. The depth of sand, between the limits of 1 and 5 ft., exercises no practical effect upon bacterial purity when

the rate of filtration is kept within the limits just specified. Thus, the New River Company, with 1·8 ft. of sand on their filters, compares favourably with the Chelsea Company, the sand on whose filters is more than twice that depth. Placed in the order of thickness of sand on their filters, the Metropolitan companies range as follows:—Chelsea, Lambeth, West Middlesex, Southwark, East London, Grand Junction, and New River. Placed in the order of efficient bacterial filtration, they range as follows:—Chelsea and West Middlesex equal, New River, Lambeth, East London, Southwark, and Grand Junction.

4. When there is such an accumulation of deposit on the surface of a sand filter that, for practical purposes, sufficient water cannot be made to pass through it, the surface of the filter has to be scraped; that is to say, mud and about half an inch of the sand are removed from the surface. After this operation there is often an increase in the number of bacteria in the filtered water, and it has been noticed that the increase is greater in shallow than in deep filters, and with high than with low rates of filtration; and there is no doubt that the effect of scraping is considerably magnified when the coarser descriptions of sand are employed, as is the case in the filters of the London water companies. I should, therefore, like to impress upon the engineers of these companies the desirability of using finer sands than are at present employed.

The lecturer here described a long series of experiments proving that the temperature of the water and the presence or absence of sunshine has little or no effect upon the number of microbes in river water, whilst the presence of flood water is almost invariably accompanied by an enormous increase in the number of microbes, showing that the microbial population of a river is directly dependent upon the volume of water flowing in its bed.

The Water Supply of the Future.

In view of the rapid increase of the population of London, fears have from time to time been entertained that the water supply from the Thames basin—that is to say, from the rivers Thames and Lea supplemented by water from springs and deep wells within the basin itself—would soon be insufficient in quantity; whilst the quality of the water taken from the river has, up to comparatively recent date, been considered unsatisfactory. On these grounds, various schemes have from time to time been brought forward for the supply of the Metropolis from other river basins: from the Wye, the Severn, the river basins of North Wales, and of the Lake Districts of Cumberland and Westmoreland. It is worthy of note, however, that all the Royal Commissions have arrived unanimously at the conclusion that the quantity of water obtainable from the Thames basin is so ample as to render the necessity of going elsewhere a very remote contingency.

I shall now endeavour to put, very shortly, before you the facts which, in my opinion, prove that, both as regards quantity and quality, the Thames basin will, for a very long time to come, afford an abundant supply for the Metropolis. There is, indeed, no river basin in Great Britain which affords such an abundant supply of excellent water as that available in the Thames basin. Besides that which flows directly into the rivers, this water is contained in the chalk, oolite, and lower greensand, which are the best water-bearing strata in the kingdom. From these strata it issues in copious springs of unsurpassed organic purity. For dietetic purposes there is no better water in the kingdom than the underground water of the Thames basin. For sentimental reasons, I should like to see it conveyed to the works of the various companies in special conduits, but we have seen that, on hygienic grounds, it may safely be allowed to flow down the bed of the Thames if it be afterwards efficiently filtered.

So much for quality, now as to quantity. The basins of the Thames and Lea include an area of upwards of five

thousand square miles. Of this, more than one-half, including the oolitic, cretaceous, and portions of the tertiary formations, is covered by a porous soil upon a permeable water-bearing stratum. The remainder is occupied by the Oxford, Kimmeridge, Gault, and London Clay; being thus covered by a clay soil upon a stiff and impervious subsoil. The annual rainfall of the district averages 28 inches. The rivulets and streams of the Thames basin are formed and pursue their course on the clay land. There are no streams on the chalk. That which falls upon the porous stratum and does not evaporate sinks, mostly where it alights, and heaps itself up in the water-bearing stratum below, until the latter can hold no more. The water then escapes as springs at the lowest available points. Innumerable examples of these springs occur all round the edge of the Thames basin, and at various points within it. Thus, from the chalk they are ejected at the lip of the gault, and in the oolitic area by the Fuller's earth below it, or by the Oxford clay, geologically, above it.

According to the gaugings of the engineer of the Thames Conservancy Board, there passed over Teddington Weir in 1892 387,000 millions of gallons, equal to an average flow of 1060 millions daily. In the following year, 1893, there passed over this weir an aggregate of 324,227 millions of gallons, or a daily average of 888 millions of gallons; the average for the two years being 974 millions of gallons, and this number does not include 120 millions of gallons daily abstracted by the five London water companies who draw their supplies from the Thames. Thus, in round numbers, we may say that, after the present wants of London have been supplied from this river, there is a daily average of nearly a thousand millions of gallons to spare. Surely it is not too violent an assumption to make that the enterprising engineers of this country can find the means of abstracting and storing, for the necessary time, one-fourth of this volume.

As regards the quality of this stored water, all my examinations of the effect of storage upon the chemical, and especially upon the bacterial, quality point to the conclusion that it would be excellent; indeed, the bacterial improvement of river water by storage for even a few days is beyond all expectation. Thus, the storage of the Thames water by the Chelsea Company for only thirteen days reduces the number of microbes to one-fifth of the original amount, and the storage of the river Lea water for fifteen days by the East London Company reduces the number, on the average, from 13,693 to 2752 per c.c., or to one-fifth. Indeed, quietness in a subsidence reservoir is, very curiously, far more fatal to bacterial life than the most violent agitation in contact with atmospheric air; for the microbes which are sent into the river above the falls of Niagara by the City of Buffalo seem to take little or no harm from that tremendous leap and turmoil of waters, whilst they subsequently, very soon, almost entirely disappear in Lake Ontario. Thus, it is not too much to expect that storage, say, for a couple of months, would reduce the number of microbes in Thames flood water down to nearly the minimum ever found in that river in dry weather; whilst, by avoiding the first rush of each flood, a good chemical quality would also be secured. There is, therefore, I think, a fair prospect that the quantity of water derivable from the Thames at Hampton could be increased from its present amount (120 millions of gallons per diem) to 370 millions.

Again, in the river Lea, although here the necessary data for exact calculation are wanting, it may be assumed that the present supply of 54 millions of gallons could be increased by the storage of flood water to 100 millions of gallons per day. To these volumes must be added the amount of deep well water which is obtainable from those parts of the Thames basin which lie below Teddington Lock, and in the Lea basin below Lea Bridge, and which was estimated by the last Royal Commission at rather more than 67½ millions of gallons. Thus we get the

grand total of 537½ millions of gallons of excellent water obtainable within the Thames basin, the quality of which can be gradually improved, if it be considered necessary, by pumping from the water-bearing strata above Teddington and Lea Bridge respectively, instead of taking the total supply from the open rivers above these points. Such a volume of water would scarcely be required for the supply of the whole water area of London at the end of fifty years from the present time, even supposing the population to go on increasing at the same rate as it did in the decade 1881—91, which is an assumption scarcely likely to be verified.

In conclusion, I have shown that the Thames basin can furnish an ample supply for fifty or more years to come; whilst the quality of the spring and deep well water and the efficiently filtered river water would be unimpeachable. To secure these benefits for the future, storage must be gradually provided for 11,500 millions of gallons of flood water, judiciously selected, in the Thames valley, and a proportionate volume in the basin of the Lea; whilst filtration must be carried to its utmost perfection by the use of finer sand than is at present employed, and by the maintenance of a uniform rate during the twenty-four hours.

The lecturer concluded as follows:—There is nothing heroic in laying pipes along the banks of the Thames or even in making reservoirs in the Thames basin; they do not appeal to the imagination like that colossal work—the bringing of water to Birmingham from the mountains of Wales; and there is little in such a scheme to recommend it to the mind of the enterprising engineers of to-day. Nevertheless, by means of storage, by utilising springs, by sinking deep wells, and by such comparatively simple means, we have, in my opinion, every reason to congratulate ourselves that, for half a century at least, we have at our doors, so to speak, an ample supply of water which, for palatability, wholesomeness, and general excellence, will not be surpassed by any supply in the world.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 6th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

Mr. J. T. Dunn was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Sidney Barwise, The Lindens, Derby; Ernest Hunter Fisher, The County Laboratory, St. Albans; William Henry Merrett, Lambeth Brass and Iron Works, Short Street, Lambeth, S.E.; Joseph W. Patterson, Esq., Avenue Road, West Hartlepool; H. von Pechmann, Tübingen, Germany; James Proude, 13, Oak Terrace, Halifax; Henry Renney, M.D., B.Sc., D.P.H., Durham, Brookfield House, Durham Road, Sunderland; Henry Fishwick Robinson, B.Sc., Sparthfield, Droydsden Road, Newton Heath, Manchester; John Henry Wolfenden, 226, Ashton Road, Failssworth, Manchester.

Of the following papers those marked * were read:—

*12. "The Molecular Weight and Formula of Phosphoric Anhydride and of Metaphosphoric Acid." By W. A. TILDEN and R. E. BARNETT.

The molecular formulæ As_4O_6 , Sb_4O_6 , P_4O_6 , $P_4O_6S_4$, and P_4S_6 , have been already established by determinations of the vapour densities of these compounds. The formula P_2O_4 has been assigned by Thorpe and Tutton to the compound they designate as phosphorus tetroxide, but no determination of the vapour density having been attempted it remains uncertain whether this formula truly expresses the molecular weight. The authors are of opinion that the low vapour density observed by V. and

C. Meyer in the case of phosphoric sulphide is due to dissociation of that compound on vaporisation into phosphorus sulphide and sulphur.

They have made a series of determinations of the density of the vapour of phosphoric anhydride at a bright red heat with results which point to the formula P_4O_{10} , instead of the simpler expression P_2O_5 , which has always hitherto been accepted, chiefly on the ground of its assumed analogy with the pentasulphide.

They have also made determinations of the density of the vapour of metaphosphoric acid, from which they draw the conclusion that this compound is partly dissociated by heat into water and the anhydride, and that the acid must be represented by the molecular formula $H_2P_2O_6$.

DISCUSSION.

Mr. DAVID HOWARD remarked that distilled metaphosphoric acid had been known commercially.

Professor THORPE observed that in the course of his work with Mr. Tutton on phosphorous oxide, he had noticed the volatility of phosphorus pentoxide, but had not been able to make use of the property, owing to the readiness with which glass was attacked by the heated substance. He agreed with the authors in believing that phosphorus pentasulphide dissociates when it volatilises, and that on this account the molecular formula P_2S_5 was open to doubt. He also concurred as to the desirability of re-determining the formulæ of many of the metallic metaphosphates.

*13. "Lead Tetracetate and the Plumbic Salts." By A. HUTCHINSON, M.A., Ph.D., and W. POLLARD, B.A., Ph.D.

In September, 1893, the authors communicated to the Society a short note on lead tetracetate (*Trans.*, lxi., 1136). Since that date the work has been extended, and the detailed results are contained in the present paper.

Lead tetracetate is obtained when red lead is dissolved in glacial acetic acid, and crystallises from the solution in monosymmetric needles, $a : b : c = 0.5874 : 1 : 0.48485$, $\beta = 74^\circ 24'$.

The specific gravity of the crystals is 2.28; they are readily soluble in chloroform and hot acetic acid, and the molecular weight determined in the latter solvent is 365 by the boiling-point method, and 408 by the freezing-point method. Lead tetracetate is decomposed by water with extraordinary ease into lead dioxide and acetic acid; acted upon by gaseous hydrogen chloride it yields lead tetrachloride, whilst if dissolved in aqueous hydrogen chloride and the solution added to a solution of ammonium chloride, the double salt, $(NH_4)_2PbCl_6$, is precipitated. When acted upon by orthophosphoric acid, lead tetracetate yields a tetraphosphate, to which the formula $Pb(HPO_4)_2$ is probably to be assigned; a propionate, $Pb(C_3H_5O_2)_4$, analogous to the tetracetate, has been prepared.

The authors point out that thallic and manganic acetates, with properties very similar to those of lead tetracetate, have been described, and give a list of salts of tetravalent lead, owing to the close analogies which exist between the stannic salts and the salts of tetravalent lead. The authors propose that the latter should be termed plumbic salts.

*14. "An Improved Method of Determining Urea by the Hypobromite Process." By ALFRED H. ALLEN.

It is well known that in the ordinary way of employing the hypobromite process for the determination of urea, the evolution of nitrogen in the form of gas is only about 92 per cent of the total nitrogen present. An increased yield of nitrogen is obtainable by adding glucose, and by certain other devices, but these modifications are open to several objections, and have not met with general acceptance.

In a paper recently read before the Society (*Trans.*, lxxvii., 746), Messrs. Walker and Hambly described some suggestive experiments on the transformation of ammonium cyanate into urea. They find that the reaction is

never complete, and they further point out that the reverse reaction occurs when an aqueous solution of urea is boiled. It follows that a solution containing both ammonium cyanate and urea ultimately arrives at a condition of equilibrium, which is upset if ammonium sulphate or potassium cyanate be added to the solution, the urea in each case being rendered more stable.

From these results it appeared probable that the incomplete evolution of nitrogen in the hypobromite process of determining urea might be due to a reversion of a portion of the urea to the condition of cyanate, especially as H. J. H. Fenton had shown (*Trans.*, xxxiii., 300) that cyanate was a product of the reaction of alkaline hypochlorites on urea, and W. Foster (*Trans.*, xxxv., 122) made the same observation with alkaline hypobromite. Fenton also found that cyanates evolved no gas when treated with alkaline hypobromite, and the author can confirm this observation. Hence it appeared possible that, by adding a sufficiency of potassium cyanate to the urea solution before adding the hypobromite, the reversion of the urea to cyanate might be entirely prevented. Experiment has proved this conjecture to be correct. An addition of 0.250 gm. of pure potassium cyanate to the solution of 0.100 gm. of urea in 5 c.c. of water, raised the evolved nitrogen from 91 to nearly 97 per cent (corr.).

If the ordinary method of operating be reversed, and instead of adding the urea solution (mixed with potassium cyanate) to a highly alkaline solution of sodium hypobromite, the cyanate be added to the solution of urea, followed by caustic soda when its solution is complete, and the bromine solution be then gradually run in, still better results are obtained. Under these conditions the yield of nitrogen is from 99.8 to 100.0 per cent (corr.). Hence the addition of potassium cyanate to the extent of two to three times the weight of the urea present effects a complete evolution of the nitrogen in the form of gas, and prevents the irregularities and uncertainty attaching to the hypobromite process in its ordinary form.

The idea of reversing the usual mode of procedure appears to have originated with J. R. Duggan (*Amer. Chem. Journ.*, iv., 47), who states that fully 99 per cent of the ureal nitrogen is evolved as gas if 5 c.c. of urine be first mixed with 20 c.c. of a solution of 20 grms. of caustic soda in 100 c.c. of water, and 1 c.c. of bromine be gradually added. I have not been able to obtain so high a yield as 99 per cent of gas without the addition of potassium cyanate, but the reversed process is in any case a valuable improvement on the ordinary method of working.

A convenient arrangement for the reversed form of the process is found in the author's work on the "Chemistry of Urine." In this apparatus a separatory funnel is substituted for the sample-tube generally used. Five c. c. of the urine or other solution of urea should be placed in the flask, and 0.250 gm. of potassium cyanate added. When solution is complete, 25 c.c. of a 40 per cent aqueous solution of caustic soda is added, the separator adjusted, and the flask connected to the nitrometer. A solution of 2 c.c. of bromine in 16 c.c. of a 20 per cent aqueous solution of potassium bromide is then added gradually from the tapped separator. The evolution of nitrogen occurs very promptly, and is usually complete by the time one-half of the prescribed volume of bromine solution has been added.

The use of silver cyanate, with or without simultaneous addition of sodium chloride, was found less satisfactory than the addition of the potassium salt.

It appeared probable that the reaction of the alkaline hypobromite with potassium cyanide would result in the formation of cyanate, in which case potassium cyanate could be conveniently extemporised in the liquid. Experiment showed that, on adding potassium cyanide to the alkaline hypobromite, great evolution of heat occurred, cyanate is formed, but the reaction appears to be complex, and the product had not the same effect as previously prepared potassium cyanate. The author intends to in-

vestigate this reaction more completely, as it does not appear to have been previously studied.

DISCUSSION.

Mr. FENTON made an experiment to show that when sodium hypochlorite reacts with urea the quantity of nitrogen evolved is only one-half of that obtained by the action of hypobromite. He had been unable to find an entirely satisfactory explanation of the fact.

Professor THORPE pointed out that Lord Rayleigh had stated that the gas evolved by the reaction of urea with alkaline hypobromite was not pure nitrogen, and suggested the desirability of examining the gas more fully.

Professor TILDEN concurred in regarding this as an important point.

Mr. HEHNER thought Mr. Allen's modified method of using this alkaline hypobromite would prove of value. He did not consider, however, that the mode of action of the potassium cyanate had been completely explained.

Mr. GROVES and Mr. PAGE remarked that the simplicity and rapidity of the hypobromite method was a strong recommendation from the clinical point of view; and Mr. PAGE pointed out that the employment of free bromine, which is required for the "reversed" process, would be a disadvantage in the wards of a hospital.

Mr. CROSS thought it would be of interest in connection with the anomalous behaviour of urea to mention that he had observed that, whilst a mixture of sulphuric acid and potassium dichromate failed to cause the evolution of nitrogen from urea, this gas is plentifully evolved if a nitrate is added to the mixture.

*15. "Preliminary Note on the Absorption of Moisture by Deliquescent Salts." By H. WILSON HAKE, Ph.D.

Some years ago the author, in experimenting with deliquescent salts, found that they exerted a desiccating action on other deliquescent salts, indicating a difference in the degree of attraction for moisture on the part of such salts.

More recently experiments were commenced with the intention of measuring, if possible, the relative degree of deliquescence, or specific deliquescence, of certain salts.

On exposing known quantities to the air, and weighing them at frequent intervals, in all cases, without exception, a maximum of deliquescence was reached in a few days, and from this point a gradual decline in weight almost invariably followed.

This maximum coincides with the formation of a definite hydrate, in a large number of cases, when the salt was pure; the water contained in it at its maximum of deliquescence approximately coincides with that required for a definite number of water molecules. As in all such cases, there was a possible margin of 1 per cent and over for the next one molecule more or less of water, the author concludes that the phenomenon of deliquescence in certain salts, and possibly other substances, is due to a tendency on their part to form a definite hydrate.

The accompanying table indicates some of the results obtained at present (see next page).

The above salts were found to be practically pure on analysis; with less pure salts an approximation to a definite hydrate was obtained, but in most cases this was sufficiently close to indicate the probable truth of the hydrate assumption.

DISCUSSION.

The PRESIDENT, Professor E. W. MORLEY, and Professor DUNSTAN commented on the fact that Dr. Hake had not so far studied the relation of the amount of absorption to the vapour pressure of water in the atmosphere to which the salts were exposed, and pointed out that until this had been done no positive conclusion could be drawn from the results.

16. "Some Derivatives of γ -Phenoxyethylmalonic Acid and of γ -Phenoxyethylacetic Acid." By W. H. BENTLEY, E. HAWORTH, and W. H. PERKIN, jun.

A.	B.	C.	D.	E.	F.	G.	H.
Substance.	Original hydration per cent.	Maximum hydration per cent reached.	Nearest molecular formula corresponding to C.	Theoretical hydration per cent corresponding to D.	Difference between theoretical and found hydration per cent.	Theoretical difference per cent for 1 mol. H ₂ O more than D.	Theoretical difference per cent for 1 mol. H ₂ O less than D.
MgCl ₂ 6H ₂ O ..	53'20	77'20	MgCl ₂ 8H ₂ O	77'33	-0'13	+0'93	-1'02
Mg(NO ₃) ₂ 4H ₂ O ..	18'18	65'89	Mg(NO ₃) ₂ 16H ₂ O	66'05	-0'16	+1'35	-1'46
CaCl ₂ 6H ₂ O ..	49'31	73'24	CaCl ₂ 17H ₂ O	73'38	-0'14	+1'10	-1'20
Fe ₂ Cl ₆ 12H ₂ O ..	39'92	66'52	Fe ₂ Cl ₆ 36H ₂ O	66'59	-0'07	+0'61	-0'63
NiCl ₂ 6H ₂ O ..	45'38	70'03	NiCl ₂ 17H ₂ O	70'18	-0'15	+1'18	-1'28
Mn(NO ₃) ₂ 3H ₂ O ..	23'17	61'54	Mn(NO ₃) ₂ 16H ₂ O	61'67	-0'13	+1'42	-1'54
H ₂ PtCl ₆ 6H ₂ O ..	20'85	47'82	H ₂ PtCl ₆ 21H ₂ O	47'97	-0'15	+1'16	-1'22
H ₂ SO ₄ ..	4'20	64'63	H ₂ SO ₄ 10H ₂ O	64'74	-0'11	+2'15	-2'43
LiCl ..	0'00	77'40	LiCl8H ₂ O	77'21	+0'19	+2'00	-2'44

γ-Phenoxyethylmalonic acid, C₆H₅O·CH₂·CH₂·CH(COOH)₂, is easily prepared by the action of C₆H₅O·CH₂·CH₂Br, β-bromethylphenyl ether, on ethylic sodiomalonate, and the hydrolysis of the resulting ethereal salt with potash. It crystallises from xylene in minute needles melting at 142° with slight evolution of gas.

γ-Phenoxybutyric acid, C₆H₅O·CH₂·CH₂·CH₂·COOH, *γ-phenoxyethylacetic acid*, is obtained by heating *γ-phenoxyethylmalonic acid* to 160–200° until the evolution of carbon dioxide ceases. It separates from light petroleum in thin plates melting at 64–65°. Heated with fuming hydrobromic acid it loses phenol, forming a bromo-derivative, which, on boiling with sodium carbonate and acidifying the product, yields butyrolactone.

Diphenoxyethylmalonic acid,—(C₆H₅O·CH₂·CH₂)₂C(COOH)₂, is obtained by acting on ethylic malonate twice with sodium and β-bromethylphenyl ether, and subsequent hydrolysis of the product with potash. It crystallises from 50 per cent acetic acid in prisms melting at 150° with decomposition.

Diphenoxyethylacetic acid,—(C₆H₅OCH₂·CH₂)₂·CH·COOH, is prepared by heating diphenoxyethylmalonic acid at 180° until carbon dioxide ceases to be evolved. It separates from light petroleum in needles melting at 88°.

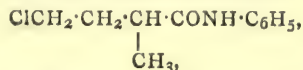
α-Phenoxyethyl-γ-hydroxybutyric acid,— $\begin{matrix} \text{HO} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{COOH}$, results on heating diphenoxyethylacetic acid with hydrogen chloride, dissolved in acetic acid for some hours at 130°. It crystallises from benzene in plates melting at 112°, and is very sparingly soluble in ether.

Ethylic-γ-phenoxyethyl-α-methyl malonate,—PhO·CH₂·CH₂·CMe(COOEt)₂, is prepared by the action of C₆H₅O·CH₂·CH₂·Br on the sodium compound of ethylic methyl malonate. It is a thick, colourless oil (b. p. 230°, pressure 45 m.m.), which, on hydrolysis, gives the corresponding dibasic acid *γ-phenoxyethyl-α-methylmalonic acid*. This acid crystallises from benzene in colourless prisms, which melt at 125° C.

γ-Phenoxy-ethyl-α-methylacetic acid is obtained by heating the previous acid at 180° till evolution of CO₂ ceases, and then distilling in a vacuum (b. p. 207°, pressure 45 m.m.). Re-crystallised from light petroleum, the acid melts at 80°. This acid was also obtained by the action of β-bromethylphenyl ether on the sodium compound of ethylic methylacetoacetate, and saponifying the resulting ether (a colourless syrup, b. p. 185°, pressure 40 m.m.) with strong alcoholic potash.

α-Methylbutyrolactone was obtained from the previous acid by first treating with aqueous hydrobromic acid, and then boiling the resulting bromo-acid with sodium carbonate solution.

The lactone was then re-converted into *γ-bromethyl-α-methylacetic acid* by treatment with HBr. This acid, which is very unstable, is a brownish, oily substance; its ethyl ether is also unstable, and could not be distilled. *γ-Chlorethyl-α-methyl acetyl chloride* was obtained as a colourless liquid (b. p. 189°) by the action of phosphorus pentachloride on *α-methylbutyrolactone*. This chloride, when acted on by aniline, gave an anilide,—



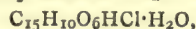
which crystallises from light petroleum in colourless prisms (m. p. 106°).

17. "Note on the Preparation of Glycol." By E. HAWORTH and W. H. PERKIN, jun.

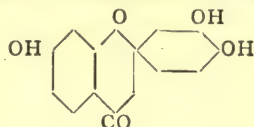
This paper describes a modification of the usual method of preparation of glycol, which consists in decomposing in a given volume of aqueous potassium carbonate, successive quantities of ethylene dibromide, by which means a concentrated solution of glycol is obtained, and subsequent loss by evaporation is reduced to a minimum.

18. "Luteolin." By A. G. PERKIN.

Luteolin, the yellow colouring-matter of Weld (*Reseda luteola*), was first isolated by Chevreul (*J. Chim. Méd.*, vi., 157), and has been subsequently investigated by others. The formula C₂₀H₁₄O₈ was assigned to it by Moldenhauer, C₁₂H₈O₅ by Schützenberger and Paraf, and C₁₅H₁₀O₆ by Hlasiwetz and Pfandl. The results here obtained agree with C₂₀H₁₄O₈ and C₁₅H₁₀O₆, and that the latter is correct is proved by the production of various derivatives. In a similar manner to quercetin, fisetin, and morin (*Trans.*, 1895, 644), luteolin combines with mineral acids, yielding the crystalline compounds C₁₅H₁₀O₆H₂SO₄, C₁₅H₁₀O₆HBr·H₂O and—



which, in contact with water, are decomposed into luteolin and the free acid. Luteolin yields a tetracetyl compound, C₁₅H₆O₆(C₂H₃O)₄, colourless needles, m. p. 213–215°, a tetrabenzoyl compound, C₁₅H₆O₆(C₇H₅O)₄, m. p. 200–201°, and a dibromo-compound, C₁₅H₈Br₂O₆, yellow needles, m. p. 303°. The acetyl compound of this latter, C₁₅H₄Br₂O₆(C₂H₃O)₄, melts at 218–220°. Rochleder has previously found that luteolin, by fusion with alkali, yields phloroglucin and protocathechuic acid, but preliminary experiments have shown that though the former is so produced, the presence of the latter could not be detected. There was, however, isolated a second substance in the form of nearly colourless needles, melting at 210°, but giving no colouration with ferric chloride. On methylation, luteolin yields a compound of the formula C₁₅H₆O₆(CH₃)₄, m. p. 191–192°. It is considered probable that luteolin is very similarly constituted to fisetin, C₁₅H₁₀O₆, or tetrahydroxy-β-phenyl-γ-pyrone, Herzig (*Ber.*, 1895, xxviii., 293),—



which it very closely resembles.

19. "An Examination of the Products obtained by the Dry Distillation of Bran with Lime." By W. F. LAYCOCK, Ph.D.

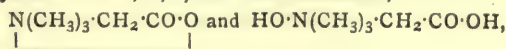
Considerable quantities of bran and unslaked lime, in the proportions of 1 : 2 by weight, were subjected to dry distillation. The resulting distillate consisted of a black oil floating on an aqueous solution. The solution contained considerable quantities of ammonia, chiefly as bicarbonate, also amines and pyrroles, together with small amounts of ketones, and ethyl alcohol.

The oil, after re-distilling, was treated with dilute hydrochloric acid, and the pyridine bases thus separated were afterwards purified. The unchanged oil was freed from small amounts of ketones by shaking with sodium bisulphite solution. The residual oil consisted of a mixture of hydrocarbons and pyrrol homologues with small quantities of furfuranes and indole.

20. "Constitution of Glycocine." By JOJI SAKURAI.

Since the publication of my paper on the "Constitution of Glycocine and its Derivatives" (*Proc. Chem. Soc.*, 137), important facts have been contributed to the history of the subject by eminent authorities, and it is interesting to observe that these new facts are either confirmatory of the ring constitution or, at least, in conformity with it.

Walker (*Proc. Chem. Soc.*, 137) has made the very important observation that glycocine is virtually a non-conductor of electricity, whilst phenylglycocine, hippuric acid, and aceturic acid are far better conductors than acetic acid, and has concluded that these glycocine derivatives must be open-chain compounds, and that, by analogy, glycocine itself has not the ring constitution. But if electric conductivity of glycocines proves anything as to their constitution it must be concluded, by the very same reasoning, that glycocine itself, being a non-conductor, cannot be an open-chain compound. A probable explanation of the difference in the electric conductivities of glycocine and its derivatives, which gives every support to the view of the cyclic constitution of the glycocines, seems obvious to me. It is that while glycocine itself appears not to form an addition compound when dissolved and, consequently, could undergo no ionisation, its derivatives do form such addition compounds, these being, as pointed out in my paper, open-chain compounds, and, therefore, capable of more or less ionisation. Betaine is an example in point which, in the anhydrous and hydrated states, is, by universal admission,—



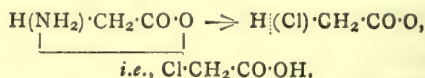
respectively.

Tilden and Forster (*Trans.*, lxxvii., 489; *Proc.*, 151) find that the primary action of nitrosyl chloride upon glycocine and several of the acid-amides is to replace the NH_2 -group by Cl; glycocine, in this manner, producing chloracetic acid. This fact they consider to be at variance with the ring formula of glycocine. The difficulty, however, does not exist. There being, as they say, complete removal of the NH_3 -group by NOCl with formation of $\text{N}_2\text{H}_2\text{O}$, and HCl , the remaining group will be $\text{CH}_2 \cdot \text{CO} \cdot \text{O}$,

and this, like ethylene oxide, will almost inevitably combine with hydrogen chloride, and produce chloracetic acid. This explanation is in conformity with that which Tilden and Forster give of the production of acetic acid from acetamide, where they assume that acetyl chloride is first formed, and then acted upon by water.

The ring formula of glycocine gives yet another explanation of the formation of chloracetic acid, and again

from Tilden and Forster's standpoint. Admitting, as they say, that by the action of nitrosyl chloride there is an interchange between NH_2 and Cl, of the divalent group, NH_3 , there will be H left along with the Cl, but hydrogen and chlorine being both monovalent, the H will go to the half-freed O, so as to give rise to chloracetic acid.



These two explanations of the production of chloracetic acid from glycocine differ only in assuming or not that hydrochloric acid has a temporary existence apart from the rest of the elements prior to the formation of chloracetic acid.

A full account of the facts supporting the theory that the glycocines are closed chain compounds is contained in the *Journal of the College of Science, Imp. Univ., Japan*.

NOTICES OF BOOKS.

Kelly's London Medical Directory, 1896, London: Kelly and Co., Limited. Pp. 519.

THE utility of this volume is not limited to the medical profession. It begins with a list of the examining bodies of London. Of these, first and foremost stands the London University, which we are duly reminded is not a teaching or still less a researching body. We hope the time may come when it may have to hand over its proud name to an organisation whose object shall be neither political nor denominational, but purely scientific.

The Local Government Board has a curious organisation. It has a staff of engineering inspectors of whom six are military men, and only three civilians. There is also a body of medical inspectors, but no chemical inspectors save the inspectors under the Alkali Acts, who, fortunately, are not soldiers.

Of course we do not censure Kelly's Directory for such a transgression against common sense. It can merely put on record facts as they exist, and leave its readers to draw the needful conclusions.

We are glad to find here the address of the Association for the Advancement of Medicine by Research,—i.e., 57, Wimpole Street. This Society is an attempt at a Biological Research Defence League, but it is deficient in confining its endeavours to medical research, and by a policy of "masterly inactivity" strikingly in contrast to that of the "anti" societies against which it should combat. We are happy to find that societies of that class are not honoured by a mention in this Directory.

In the main portion of the work before us, which gives the names and addresses of legitimate medical practitioners in London and its district, we find what to us appears a needless prolixity. Attached to many names of physicians and surgeons we find not only the degrees which they have taken, the learned societies to which they belong, and the works which they have written, but communications which they have addressed to various journals, and the names of ships on which they have sailed in their professional capacity.

It is highly desirable that ships' surgeons should be appointed not by the owners of the vessels, but by a national authority. At present the more thoroughly a ship's surgeon does his duty, the more doubtful is his term of office.

In the street directory, N. district, we see an omission of Tollington Park, in which several qualified practitioners reside.

Among the hospitals we are not able to find that for fevers in Liverpool Road, Islington.

Altogether, "Kelly's Medical Directory" will be found very widely useful.

Computation Rules and Logarithms, with Tables for other Useful Functions. By SILAS W. HOLMAN, Professor of Physics at the Massachusetts Institute of Technology. New York and London: Macmillan and Co. 1896. Pp. 73.

THIS work contains tables of logarithms to four and five places, besides square roots and squares, four place reciprocals, slide wire ratios, natural sines and cosines, natural tangents and cotangents, all four place, besides five place logarithms of sines, cosines, tangents and cotangents, and certain useful constants.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 5, February 3, 1896.

Observations on G. Le Bon's recent Paper on Dark Light.—G. H. Nievenglowski.—Already inserted.

Photography by Dark Light.—Gustave Le Bon.—Already inserted.

New Properties of the X Rays.—L. Benoist and D. Hurmuzosou.—Already inserted.

Experiments with Röntgen's Rays.—Albert Nodon.—Already inserted.

Permeability of Metals for the X Rays.—V. Chataud.—Already inserted.

The Photography of Metallic Objects through Opaque Substances by means of the Brush and the Induction Coil, without the Crookes Tube.—G. Moreau.—Already inserted.

Fluorides of Acids.—M. Meslans and F. Girardet.—The fluorides of acids are very easily obtained, and with yields nearly theoretical in quantity, by the action of the chlorides of acids upon zinc fluoride. These substances rapidly attack glass in presence of traces of water. In presence of this latter body they display a greater stability than the chlorides; they do not fume in the air; they react slowly with the alcohols to form ethers, and rapidly with ammonia to form the corresponding amides.

Preparation of the Fluorides of Acids.—Albert Colson.—The author has obtained and examined the fluorides of acetyl and propionyl.

On a Lithium Hydride.—M. Guntz.—This compound has the well-defined composition LiH. If heated in a current of nitrogen, the hydride is decomposed with the formation of a nitride. In a current of air it burns with the formation of lithia. The stability of lithium hydride at a red heat, its composition, its aspect, and its properties, quite distinct from the potassium and sodium hydrides, show a new distinction between the properties of lithium and those of the alkaline metals.

Journal für Praktische Chemie,
New Series, Vol. li., Parts 10 and 11.

Researches from the Chemical Institute of the University of Kiel.—These consist of the continuation of a memoir by C. Stoehr on the pyrazines and the piperazines. On comparing the three substances pyrazin, pyridin, and benzene, closely related in their constitution, it appears that with an increase of the molecular weight, the specific gravities increase and the boiling-points rise. On hydration, there does not occur successive change in the boiling-points, because the hexahydro-products of benzene and pyridin boil at a lower point than their fundamental substances, whilst with pyrazin the relation is inverse.

Researches from the Laboratory of the University of Freiburg, in Breisgau.—These researches comprise

a paper by Ad. Claus and Ann. Caroselli on orthoparadi-bromquinolin.

Conversion of Ketones into α -Diketones.—M. Filetti and G. Ponzio.—In a former paper the authors expressed a suspicion that the diketone is not formed by direct oxidation of the ketone. Subsequent experiments have shown that their conjecture is justified.

Derivatives of Metamethylorthouramidobenzoyl.—St. von Niementowski.—An account of carboxethyl-orthoamidoparatoluyamide, of nitrometamethylorthouramidobenzoyl, of amidometamethylorthouramidobenzoyl, of dinitrometamethylorthouramidobenzoyl, of diamidometamethylorthouramidobenzoyl, and of the diacetyl derivative of diamidometamethylorthouramidobenzoyl.

Analogy in the Behaviour of Halogen Alkyls with Sodium and analogous Metals on the one side and the Mercaptides on the other.—R. Otto and K. Mühle.—As far as the present experiments extend, all halogen-alkyls with fewer than 4 atoms of carbon yield alkylenes both with sodium mercaptides and with sodium.

Constitution of the η -Phenylpyrazolones.—R. von Rothenburg.—A controversial memoir against F. Stolz, L. Claisen, and E. Haase.

Diamidobenzoic Acids.—C. Haeusserrmann and H. Teichmann.—An account of the ethyl-ester of 3.5-diamidobenzoic acid.

Constitution of Diazobenzene Compounds.—R. Walther.—It is clear that identical substances must be formed from diazobenzene and bromaniline on the one hand; and, on the other hand, from diazobrombenzene and aniline. It is manifest how, from one and the same diazobenzene, sometimes azo- and sometimes hydrazo-compounds are formed according to the ingredients to be combined.

MEETINGS FOR THE WEEK.

MONDAY, 2nd.—Society of Arts, 8. (Cantor Lectures). "Chemistry of certain Metals and their Compounds used in Building, and the Changes produced in them by Air, Moisture, and Noxious Gases, &c.," by Prof. J. M. Thomson, F.R.S.E.

Medical, 8.30.

Medical and Chirurgical, 8.30. (Anniversa y).

Society of Chemical Industry, 8. "Artificial Silk," by Messrs. Cross and Bevan.

TUESDAY, 3rd.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.

Society of Arts, 8. "The Commercial Prospects of English East Africa, and British Central Africa," by G. Scott Elliott.

Institute of Civil Engineers, 8.

Pathological, 8.30.

WEDNESDAY, 4th.—Society of Arts, 8. "Röntgen's Photography of the Invisible," by A. A. Campbell Swinton.

Society of Public Analysts, 8. "Estimation of the Diastatic Power of Malt," by Walter J. Sykes, M.D., and C. A. Mitchell, B.A. "Further Note on the Detection of Formalin," by H. Droop Richmond and L. K. Boseley. "The Detection of Formalin," by Otto Hehner. "Note on the Detection of Cotton-seed Oil in Lard," by E. J. Bevan.

THURSDAY, 5th.—Royal, 4.30.

Royal Society Club, 6.30.

Royal Institution, 3. "Masters of Modern Thought—I. Voltaire," by The Rev. W. Barry, D.D.

Chemical, 8. "On the Explosion of Cyanogen," by H. B. Dixon, E. H. Strange, and E. Graham. "On the Mode of Burning of Carbon," by H. B. Dixon. "On the Detonation of Chlorine Peroxide," by H. B. Dixon and J. A. Harker. "The Constitution of a New Acid resulting from the Oxidation of Tartaric Acid," by H. J. H. Fenton.

FRIDAY, 6th.—Royal Institution, 9. "The Tunnel under the Thames at Blackwall," by A. R. Binnie, M.Inst.C.E.

Geologists' Association, 8.

Quekett Club, 8.

SATURDAY, 7th.—Royal Institution, 3. "Light," by Lord Rayleigh, F.R.S., &c.

Medical, 7. (Annual Dinner).

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1893.

ON THE DEPRESSION OF EXPLOSIVE POTENTIALS, STATIC AND DYNAMIC, BY THE X RAYS.

By M. R. SWYNGEDAUF.

THE analogy between the ultra-violet rays and the Röntgen rays has led me to try the action of the latter upon the explosive potentials. Experiment has shown that the X rays lower explosive potentials according to the same general laws as the electrically active ultra-violet radiations.

The depression of the static explosive potentials is measured directly with the electrometer of Bichat and Blondlet, noting the explosive potential of the exciter, when illuminated by the rays or not illuminated.

The Crookes tube is traversed by the discharge of a Ruhmkorff coil actuated by two accumulators; it is placed parallel to the exciter, and at the distance of 25 c.m. from the latter. The exciter is formed of two iron spheres of 1 c.m. in diameter.

In an experiment where the explosive distance is 5½ metres, the exciter is discharged for a potential of 60 C.G.S. units, if not illuminated by the X rays. Under the influence of these rays the spark strikes at a potential of 58·8 C.G.S.

A black paper, a plate of glass or of wood, do not change, in an appreciable manner, the depression of the explosive potential.

A plate of brass, of the thickness of 0·5 m.m., completely suppresses the explosion.

The depression of the dynamic explosive potential is measured by the method of the two derived exciters formerly described (*Comptes Rendus*, Feb. 3, 1896). For the arc-lamp we substitute the Crookes tube; we place an opaque screen for the radiation (e.g., a plate of brass), between the two derived exciters, $E_1 E_2$ and $N_1 N_2$.

Still in this form the method gives only negative results. This depends on the fact that the illumination with the Crookes tube is necessarily intermittent, and lasts only for a very small fraction of a second; a very fortunate coincidence is required, for the tube to be illuminated at the moment of the dynamic charge of the exciters.

To evade this difficulty I employ an artifice by means of which the Crookes tube is illuminated at the same time as the derived exciter is charged by the dynamic method (discharge of the condenser, GC_2).

In the secondary circuit of the Ruhmkorff coil we place a Crookes tube and a secondary exciter, S. This exciter is placed at the distance of 4 c.m., and opposite the poles of the principal exciter, $I_1 I_2$, which allows the charge of the condenser. The Crookes tube is placed opposite $E_1 E_2$, at the distance of about 25 c.m.

We actuate the Ruhmkorff coil; at each spark which strikes in S the coil discharges itself through the Crookes tube.

We charge the condenser slowly with a Holtz machine; when the potential of the exciter $I_1 I_2$ is close upon its static explosive potential, the one of its sparks which hurls in S excites, by its ultra-violet radiations, the discharge of the exciter $I_1 I_2$ and of the condenser, and the derived exciters $E_1 E_2$ and $N_1 N_2$ are charged dynamically; $E_1 E_2$ are two rings of iron of 1 c.m. in diameter; $N_1 N_2$ are two rings of brass, also of 1 c.m. in diameter.

If $N_1 N_2 = 3$ m.m., the spark still bursts at $E_1 E_2$ when the explosive distance of $E_1 E_2$ is 5·40 m.m. under the influence of the X rays.

In the absence of these rays the poles of $E_1 E_2$ must be brought to the distance of 3 m.m., so that the spark may burst at $E_1 E_2$ rather than at $N_1 N_2$.

The interposition of a screen of paper or of glass does not diminish the depression in an appreciable manner. A plate of brass suppresses it entirely.

The spark of the same Ruhmkorff coil produces a lowering of the same order of magnitude if no screen is interposed between the exciter and the spark. A screen of wood, glass, or black paper arrests the active ultra-violet rays.

From these experiments we shall draw the following conclusions:—

I. When measuring the depression of the dynamic explosive potentials by the method of the derived exciters, we may detect with great distinctness the X rays.

II. The Röntgen rays lower the dynamic explosive potentials in much greater proportions than the static potentials.

—*Comptes Rendus*, cxxii., p. 374.

ELECTRICAL PHENOMENA PRODUCED BY THE RÖNTGEN RAYS.

By A. RIGHI.

In the *Comptes Rendus* for February 3rd I find a communication, by MM. Benoist and Hurmuzescu, on the dissipation of electric charges obtained by the Röntgen rays. As I have executed similar researches at the same time as these physicists, and have communicated them to the Academy of Sciences of Bologna at its last Session, and as my results are not entirely identical with those of Benoist and Hurmuzescu, I solicit permission to give here a summary.

I have used a Mascart electrometer as a measuring apparatus. It is in connection with the substances upon which the X rays are caused to fall, and which emanate from a Crookes tube enclosed along with the apparatus yielding the discharges in a large metal case connected with the earth. The part of the case which is close to the tube is formed of a thick sheet of lead, having in the middle a round window of 1 c.m. in diameter, covered with a slender plate of aluminium, whence the rays issue.

I have found that a metallic disc communicating with the electrometer rapidly loses its charge, whether positive or negative. The duration of action necessary for the potential to fall from 7 to 3·5 volts is sensibly alike for a positive and for a negative potential.

With an initial positive charge the discharge is not complete; with a negative the substance is not merely discharged, but there is formed a positive charge.

If I cause the Röntgen rays to fall upon one of my photo-electric couples which are formed of a metallic tissue in connection with the earth, parallel and very near to a metallic disc in connection with the electrometer, I obtain deviation which is positive or negative, according to the nature of the metals of the couple, as with the ultra-violet rays.

A disc in its natural state is charged positively, if exposed to the new radiation (which takes place also on employing the ultra-violet rays). With this same disc the final positive potential is the same, whatever may be the initial value of the potential of the disc—positive, negative, or null. This final potential is higher for copper than for zinc, and still higher for retort-coke.

I find, besides, that a plate of glass, being nearly 1 c.m. in thickness, if placed on the path of the X rays, does not destroy their action, but enfeebls it appreciably. In the same manner the interposition of a thick plate of aluminium, or a thick board of deal, or even of the hand laid so as completely to cover the window, merely en-

feeble more or less the action of the rays. I expect that similar results will have been obtained by other physicists. —*Comptes Rendus*, cxxii., p. 376.

ACTION OF THE RÖNTGEN RAYS ON ELECTROSTATIC CHARGES, AND ON THE EXPLOSIVE DISTANCE.*

By J. J. BORGMAN and A. L. GERCHUN.

J. J. THOMSON has communicated to the readers of the *Electrician* (Feb. 7, 1896) an observation concerning the effect of the Röntgen rays upon electrostatic charges. According to him positive and negative charges are equally dissipated by the action of the rays. Our experiments do not completely confirm this fact.

A disc of zinc connected to an electroscope of medium sensitiveness and charged positively lost its charge almost instantly under the action of the Röntgen rays emanating from a Crookes tube at a short distance. For greater distances (1 metre) the dissipation of the charge still continues, but more slowly. After the loss of the positive charge, the leaves of the electroscope diverge anew, and indicate a negative charge, which goes on increasing up to a certain degree. If we communicate to the disc a negative charge the electroscope shows a much slower loss, which stops at a certain degree. The loss was smaller for low distances, and became moderately large if we removed the disc from the tube. When the stationary divergence of the electroscope was reached, the angle of divergence oscillated continually, becoming sometimes smaller, sometimes larger, according to the irregular progress of the interrupter. A leaf of aluminium (1 m.m. in thickness), connected with earth, weakened the action of the rays without altering their character. These experiments seem to show that the rays issuing from a Crookes tube may communicate a negative charge to the conductors.

In another experiment the rays fell upon two small platinum balls connected with a small Ruhmkorff apparatus. The distance of the balls was too great for a spark to overleap, yet the Röntgen rays falling upon the exciter produced immediately a lively projection of sparks. A thin leaf of aluminium connected with the earth, or plates of ebonite placed in the course of the rays, did not perceptibly modify the action. This experiment seems to prove that the Röntgen rays, like the ultra-violet rays, may increase the explosive distance of a static discharge. —*Comptes Rendus*, cxxii., p. 375.

NATURE AND PROPERTIES OF DARK LIGHT.

By GUSTAVE LE BON.

BEFORE speaking of the new results of my researches I have the honour of informing the Academy that my experiments on the passage of ordinary light through opaque bodies have been repeated with full success by some observers, especially by Dr. Armeniac, of Bordeaux, and H. Murat, of Havre. The latter, following exactly my instructions, has succeeded in obtaining with the dark light results superior to those produced by the Röntgen rays.

The dark light and the rays of cathodic origin are certainly not similar radiations, for the dark light does not traverse substances such as ebonite, which are quite transparent to the Röntgen rays. M. Murat has sent me photographs of the inside of a fish, which I have the honour of presenting to the Academy. They show a sort

of successive dissection, layer by layer, such as I will explain in a future communication. The light of a simple lamp transformed into dark light by the procedure which I have indicated, that is to say, by its passage through the metallic plates, sufficed to obtain these results.

In my former papers I wished to publish only the crude results of my experiments. They seemed so inexplicable that it is necessary to indicate the theory which led me to execute them, and which permitted me to foresee them.

My purpose was to explore the region, still unknown, which separates the region of light from that of electricity. I supposed, as I said at the end of my first memoir, that the forms of energy should be infinite in number. We know merely a few, such as heat, light, and electricity. But these known forms should be connected together by intermediate forms; these latter are still unknown, because we do not possess instruments capable of translating them in a manner perceptible to our senses.

In order to discover one of these modes of intermediate energy, we must first find an instrument capable of showing vibrations less numerous than those of light and more numerous than those of electricity. Photographic plates being under certain conditions still sensitive to the vibrations relatively few in number situate beyond the visible spectrum, it was to be hoped that they might be sensitive to vibrations much more numerous. If it were really thus we should find ourselves exactly in the zone intermediate between light and electricity. But then this new form of energy ought to possess some properties intermediate between light and electricity. It would perhaps not propagate itself like light, and perhaps might propagate itself like electricity. In this latter case the vibrations should not be arrested by opaque metallic bodies, whatever their thickness. To verify these conceptions I devoted researches pursued during two years, and I wished to expound in my first paper merely the most incontestable results. Without the theory which guided us we should have been arrested by the failures which attended our first researches.

The demonstration of the passage of light through thick plates of metal was effected very rapidly, but the results were attended with partial failures, which embarrassed me for a long time. Most frequently the image was perfect at the external margins of the plate, or at its centre, and then suddenly stopped. On employing two metals we either promoted or hindered the experiment. It is thus, for instance, that the presence of a sheet of polished tin behind the sensitive plate decidedly hinders the passage of the light through the plate of aluminium covering the proof. Sometimes very satisfactory results were obtained on placing the glass before or behind the proof. Sometimes the image was negative and sometimes positive. Evidently electric influence must intervene, but no less evidently the effects produced were due to the action of light, since, all the conditions of the experiments being alike, the images were obtained only when the light fell upon the opaque plates covering the frame. In a future note I will explain how, by means of an instrument infinitely sensitive (a galvanometer with a frame movable, in an intense magnetic field produced by an auxiliary current of 30 volts and 2 amperes), I hope to demonstrate the liberation of electricity during the formation of ordinary photographic images. At present I wish to explain merely the experiments concerning the passage of light through opaque bodies and the transformations which it then undergoes.

In the experiments which are to follow each proof receives two sensitive plates, one on its upper part and one on its lower part: one of them serves as a check,—that is, it shows by a previous sojourn of the fitted frame in darkness, that the image produced on the plate covering the second part of the proof is produced only under the influence of the dark light. In this manner we totally eliminate all hypotheses which might be formed on the causes of the formation of the image,—light stored up, pressure, heat, electricity, &c. Only the light which has

* Compare with paper by R. Swyngedauw (see p. 109).

traversed the plate, and has been transformed into dark rays, produces the image, since without such light the image is never produced.

Now follow a series of experiments which would seem very contradictory if we had not, for their explanation, the theory which I have propounded, and if we consider that the dark light must, like ordinary light, always propagate itself in a right line.

The frame being covered with one of the metals which I have indicated—for instance, iron or aluminium—one-half of the metal plate is covered with about ten leaves of paper superimposed, which will suffice, with the exposure which we employ, to arrest the formation of the image on a sensitive plate exposed beneath a proof. Now on developing we find that the image is absolutely equal in intensity both under the part covered merely by the metal and in the part where the metal itself is covered with ten thicknesses of paper. If upon this same metal plate we superimpose larger discs of iron, of several centimetres in thickness, we still find that these discs, notwithstanding their thickness, leave no trace upon the image.

These experiments, which have been repeated and modified in every way, are fundamental. They show us at first that the degree of thickness of the opaque plates is without importance for the passage of light, just as it would be for the passage of electricity. The experiments show us that dark light in its propagation follows other laws than those of ordinary light. In fact, if dark light were propagated in a right line, the parts of the proof protected by the discs and the leaves of paper placed upon the metal plates would be indicated by a shadow on the glass. But if the dark light obeys the laws of propagation of electric waves, if one point of the metal receives the rays they are propagated over the entire surface.

We may thus transform light into radiations which are propagated like electric currents. Still they are not electric radiations, since ordinary electric currents do not produce the same effect.

We find ourselves thus in presence of a mode of energy which is no longer light, since it has only a part of its properties and does not obey its laws of propagation. Neither is it electricity, since electricity in its known form does not produce the same effects. Dark light must probably be considered as a new force in addition to the small number already known.—*Comptes Rendus*, cxxii., p. 386.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, February 10th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Jan. 1st to Jan. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined one was recorded as "clear but dull," the remainder being clear, bright, and well filtered.

The rainfall at Oxford during the month has been 0.63 inch, as against 2.16 inches, the average for the past 29 years; this shows a deficiency of 1.53 inches, as compared with the average.

The exceptionally small rainfall in the Thames Valley during January has improved the condition of the river and made filtration operations remarkably effective.

The quality of the supply during the past month, regarded both from the chemical and bacteriological point of view, has been exceptionally good.

Our bacteriological examinations for the month of January give the following numbers of colonies per cubic centimetre:—

	Colonies per c.c.
Thames water, unfiltered	1824
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	50
Ditto ditto lowest	24
Ditto ditto .. (12 samples) mean	36
New River water, unfiltered	1525
New River water, from the Company's clear water well	31
River Lea water, unfiltered	2005
River Lea water from the East London Com- pany's clear water well	24

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

THE WALRAND-LEGÉNEL PROCESS FOR STEEL CASTINGS.

By SERGIUS KERN, M.E. St. Petersburg.

In 1894, Mr. George Snelus, F.R.S., read a paper under this heading at the May meeting of the Iron and Steel Institute in London. The paper gave an elaborate statement of the working of small Bessemer converters, at Paris and Hagen, by the Walrand-Légénéel method.

At the Franco-Russian Works, St. Petersburg, this process was lately started, with good success, by the inventors. We witnessed five operations, consecutively made, in one afternoon. The converter is for a charge of 300 kilos., which is run from a Walrand cupola, working very regularly, and consists of Ayresome pig-iron, scrap (runners, top-ends, &c.), and a small quantity of ferro-silicium, in order to have in all 3 to 3.15 per cent of silicon in the metal to be converted into steel.

At a certain time during the third period of the Bessemer process a charge of ferro-silicium was added, an afterblow made, and, finally, silicospiegel added.

The resulting steel is poured into ladles, into which about 0.1 per cent of metallic aluminium is thrown.

The steel is hot and readily fills the mouldings. The metal in the castings is soft and ductile. In order to give an idea of the *modus operandi*, we took the following notes:—

First blow, commenced at 1.51 p.m.; metal from fourth blow poured into moulds at 4.5 p.m. So that in two hours fourteen minutes four blows were made.

Description of the first blow, which was the coldest of all, being the commencement of operations:—

1. Pig-iron poured into the converter, and blow commenced at 1.51 p.m. (pressure of air about 32 lbs.).

2. Commencement of the second period, line D of sodium well marked, 2.2 p.m. (pressure of air about 15 lbs.).
3. Converter turned, to add ferro-silicium, and commencement of afterblow at 2.8½ p.m. (pressure of air, 22 to 24 lbs.).
4. Silicospiegel added at 2.10½ p.m.
5. Commencement of the pouring of steel into ladles, 2.14 p.m.

The same process, but with two (nearly one ton each) converters, has been started also at the Baltic Ship-building Works, St. Petersburg, and with encouraging success.

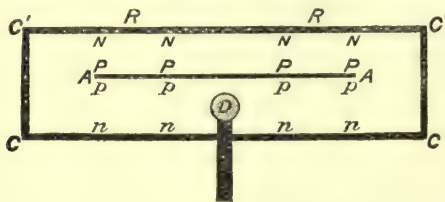
We remarked only that for small castings up to 100 to 150 kilos. crucible steel is more useful, being a little colder, with less gases in solution, and therefore more quiet. It better fills the small mouldings attached to a general runner.

Having seen the practice of the new process, we find it specially adapted to large and medium sized castings. Sometimes, as a result of working, very small castings are shown in order to popularise new processes, but one must believe that in such a case the small castings are picked out of series of similar articles, bad ones being rejected.

ON THE GENERATION OF LONGITUDINAL WAVES IN ETHER.*

By Lord KELVIN, F.R.S.

In a short note recently published in *Nature*, of which a copy is appended, I suggested an arrangement of four insulated and electrified spherical conductors with their centres in one line, giving rise to ethereal waves in the surrounding atmosphere, of which the disturbance in the line of centres is essentially longitudinal. But at any finite distance from this line there must also be laminar or distortional waves of the kind expressed in Maxwell's equations. The object of my present communication is to show an arrangement by which a large space of air is traversed by pressural disturbance, or by waves essentially longitudinal, or by condensational-rarefactional vibrations; with but a very small proportion, practically evanescent, of laminar waves.



Let AA be a plane circular metal plate insulated within a metal case, CC C' C'', as indicated in the drawing. Let D be a discharger which can be pushed in so as to make contact with A.

Let A be charged to begin with, positively for instance as indicated by the letters P P P P; N N N N showing negative electricity induced by it. Let now the discharger be pushed in till a spark passes. The result, as regards the space between AA and the roof RR over it, will be either an instantaneous transmission of commencement of annulment of electrostatic force, or a set of electric waves of almost purely longitudinal displacement, according as ether is incompressible or compressible.

Hence, if the theory of longitudinal waves, suggested by Röntgen as the explanation of his discovery (for the consideration of which he has given strong reasons), be true, it would seem probable that a sensitive photographic

plate in the space between AA and RR should be acted on, as sensitive plates are, by Röntgen rays. Either a Wims-hurst electrical machine or an induction-coil, adapted to keep incessantly charging AA with great rapidity, so as to cause an exceedingly rapid succession of sparks between D and A, might give a practical result. In trying for it, the light of the sparks at D must be carefully screened to prevent general illumination of the interior of the case and ordinary photographic action on the sensitive plate.

The arrangement may be varied by making the roof of sheet aluminium, perhaps about a millimetre thick, and placing the sensitive photographic plate, or phosphorescent substance, on the outside of this roof, or in any convenient position above it. When a photographic plate is used there must, of course, be an outer cover of metal or of wood, to shut out all ordinary light from above. This arrangement will allow the spark gap at D to be made wider and wider, until in preference the sparks pass between AA and the aluminium roof above it. The transparency of the aluminium for Röntgen light will allow the photographic plate to be marked, if enough of this kind of light is produced in the space between the roof and AA, whether with or without sparks.

The new photography has hitherto, so far as generally known, been performed only by light obtained from electric action in vacuum; but that vacuum is not essential for the generation of the Röntgen light seems demonstrated by an experiment by Lord Blythwood, which he described at a meeting of the Glasgow Philosophical Society on February 5th. As a result he exhibited a glass photographic dry plate with splendidly clear marking which had been produced on it when placed inside its dark slide, wrapped round many times in black velvet cloth, and held in front of the space between the main electrodes of his powerful Wims-hurst electrical machine, but not in the direct line of the discharge. He also exhibited photographic results obtained from the same arrangement, with only the difference that the dark slide, wrapped in black velvet, was held in the direct line of the discharge. In this case the photographic result was due, perhaps wholly, and certainly in part, to electric sparks or brushes inside the enclosing box, which was, as usual, made of mahogany, with metal hinges and interior metal mountings. I have suggested to him to repeat his experiments with a thoroughly well-closed aluminium box, instead of the ordinary photographic dark slide which he used, and without any black cloth wrapped round outside. The complete metallic enclosure will be a perfect guarantee against any sparks or brushes inside.

If the arrangement which I now suggest, with no sparks or brushes between AA and the roof, gives a satisfactory photographic result, or if it shows a visible glow on phosphorescent material placed anywhere in the space between AA and the roof above it, or above the aluminium roof, it would prove the truth of Röntgen's hypothesis. But failure to obtain any such results would not disprove this hypothesis. The electric action, even with the place of the spark so close to the field of the action sought for as it is at D, in the suggested arrangement, may not be sudden enough or violent enough to produce enough of longitudinal waves, or of condensational-rarefactional vibrations, to act sensibly on a photographic plate, or to produce a visible glow on a phosphorescent substance.

Extract from *Nature*, referred to above:—

"Velocity of Propagation of Electrostatic Force.

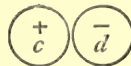
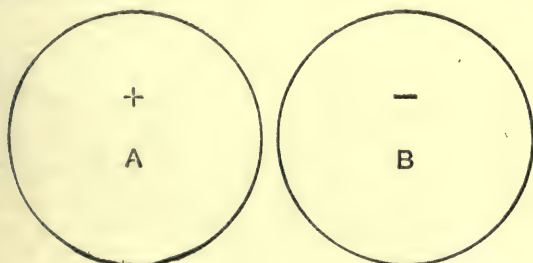
"Dr. Bottomley's note published in *Nature*, of Jan. 23, quotes an extract from my Baltimore Lectures of October, 1884, in which this subject is spoken of, with an illustration consisting of two metal spheres at a great distance asunder, having periodically varying opposite electrifications maintained in them by a wire connecting them through an alternate current dynamo.

"For an illustration absolutely freed from connecting

* A Paper read before the Royal Society, February 13, 1896.

wire and all complications, consider four metal spheres, A, B, C, D, with their centres all in one straight line; their relative magnitudes and positions being such as shown in the accompanying diagram. Let each of the four be initially electrified, A and C positively, B and D negatively. Let the charges on C and D be so strong that a spark is only just prevented from passing between them by the influence of B and A. Let A be gradually brought nearer to B till a spark passes between them. Will the consequent spark between C and D take place at the same instant or a little later? It is not easy to see how this question could be answered experimentally; but remembering the wonderful ingenuity shown by Hertz in finding how to answer questions related to it, we need not, perhaps, despair to see it also answered by experiment.

"The elastic solid theory restricted to the supposition of incompressibility (which is expressed by Maxwell's formulas) makes the difference of times between the two sparks infinitely small. The unrestricted elastic solid theory gives for the difference of times the amount calculated according to the velocity of the condensational-rarefactional wave.



"But I feel that it is an abuse of words to speak of the 'elastic solid theory of electricity and magnetism,' when no one hitherto has shown how to find in an elastic solid anything analogous to the attraction between rubbed sealing-wax and a little fragment of paper; or between a loadstone or steel magnet and a piece of iron; or between two wires conveying electric currents. Elastic solid, however, we must have, or a definite mechanical analogue of it, for the undulatory theory of light and of magnetic waves and of electric waves. And consideration of the definite knowledge we have of the properties of a real elastic solid, which we have learned from observation and experiment, aided by mathematics, is exceedingly valuable in suggesting and guiding ideas towards a general theory which shall include light (old and new) old and new knowledge of electricity, and the whole of electro-magnetism.—KELVIN."

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 90.)

On the Flame Spectrum of Chloride of Calcium.—I checked the spectrum of pure oxide by reducing it to chloride. In the previous chapter I described the method by which I obtained the chloride of calcium used in the first experiment.

After having heated to redness, long enough to drive off sodium brought by the air, a thin concave sheet of platinum containing a cone of spongy iridium, I poured over the cone enough fused chloride of calcium to thoroughly soak it. I then projected on to the top of the cone the point of an oxyhydrogen blowpipe, in which spectrum analysis only showed very transient traces of the sodium D line. At the very moment of contact I

saw the sodium line of remarkable strength, but it became weaker until there was nothing but a trace seen in the blowpipe flame in air: this happened when the chloride was so far dissociated that it had become an oxychloride, infusible at the fusing-point of platinum.

When, instead of heating the chloride of calcium in an oxyhydrogen blowpipe on a cone of spongy iridium, it is fused on to an iridio-platinum loop overlaid with sodium, or on to a hook of iridium alloyed with 20 per cent of platinum, or on to a small cone of pure carbon ending in a point, and if the loop, hook, or needle-point thus coated were introduced into the envelope of an oxyhydrogen or oxy-coal-gas blowpipe, spectrum analysis shows the sodium line at once, *strongly at first*, but gradually getting fainter until it is no stronger than it is seen in a blowpipe without the chloride.

The spectrum of oxide of calcium exhibits a remarkable constancy of position. From the moment of its appearance in an oxyhydrogen or oxy-coal-gas blowpipe, until the highest temperature attainable by burning hydrogen in oxygen is reached, no matter whether there be more or fewer bands and hazy lines, or whether the back-

ground be dark or shows a continuous luminous spectrum, the position of the bands and lines is absolutely the same. The flame spectrum of chloride of calcium acts quite differently. Up to the moment of greatest luminosity, which appears to coincide with the spectrum of the chloride itself, the bands, although distinct, are very hazy, possibly owing to the width of the slit; they appear to me to be in a permanent state of slight undulation until the chloride is completely reduced to oxychloride or oxide of calcium, or at least until the gases and vapours in the air cease to smell of chloride of calcium and hydrochloric acid and begin to smell of oxide of calcium.

On account of the dissociation of chloride of calcium in an oxyhydrogen or oxy-coal-gas flame, I consider the use of the blowpipe much less suitable with chloride than with oxide, and especially with granular oxide, for observing the lines characteristic of the flame spectrum of calcium, much less for measuring the position of these lines.

I frequently noticed that, at the instant of introducing chloride of calcium into the hottest part of the blowpipe, the compound became incandescent, and emitted white light; this afterwards became bluish white. The calcium colour only appeared in the blowpipe at a considerable distance from the point of introduction. This phenomenon is not seen when using oxide or sulphate of calcium instead of chloride of calcium, on an iridio-platinum loop overlaid with pure iridium. When using oxide made by calcining nitrate of calcium, the flame was deep brownish red or chocolate colour, from the instant the compound was volatilised in any part of the flame. It appears, then, that the emission of the bluish white light coincides with the dissociation of the chloride.

In order to ascertain exactly the cause of the appearance of the sodium line with the chloride, I repeated the experiments, using, instead of the blowpipe, a spark and discharge from an induction-coil *without* and with a condenser. I thus found that the colour of the spark varied with the amount of chloride of calcium used, and that

the sodium line was a little fainter than when using the blowpipe.

This line persisted with the same relative intensity throughout the experiments, and was *stronger* than that seen at the same time in the surrounding air, when substituting *uncovered* balls of pure platinum for those covered with fused chloride of calcium, whether *anhydrous* or *moistened* with a saturated solution of the compound.

It undoubtedly follows from these observations that, during the conversion of oxide into chloride of calcium, and, I may add, throughout the experiment in air containing sodium, the compound occludes sodium in spite of my extreme care. I must add, to be accurate, that during these researches the state of the air was not all that could be wished for. The hygroscopic quality of chloride of calcium doubtless aided in attracting the sodium. I proved that, on evaporating water, condensed from the air in which I was working, collected on the outer surface of a platinum dish containing ice, the residue left contained an appreciable amount of sodium. Besides, the facts I have yet to describe will prove that the presence of sodium is *solely* due to this cause.

I have submitted to spectrum analysis a spark flashing from the surface of a hydrochloric solution of chloride of calcium, made from elements free from sodium, in the tube which held it, in pure air.

With this object I distilled with the greatest care, on the one hand, a 10 per cent solution of hydrochloric acid in a platinum apparatus filled with purified air. After distilling it, I closed the receiver by a platinum plug fitted to the tube.

Spectrum analysis of a Bunsen flame, into which I gradually introduced by means of a platinum tube about 1 c.c. of the condensed acid, *did not show the sodium line.*

On the other hand, I made some pure oxide of calcium, by projecting into some carbonate of calcium, on a recently heated sheet of platinum, a coal-gas and air blow-pipe flame, until spectrum analysis of the calcium flame ceased to show the sodium line. The accidental traces of sodium being completely eliminated, I at once put the sheet of platinum with the oxide under a small glass bell-jar full of purified air, with its rim ground and greased, standing on a sheet of smooth and polished glass, and I took the whole into the large room devoted to spectroscopic work.

Having heated to whiteness a small platinum dish containing a hollow cone, the top of which was about 2 m.m. below the edge of the dish, I poured over it a suitable quantity of oxide of calcium, and I put the dish with the oxide on the three-pronged support of the small apparatus* intended to saturate an electric spark or discharge with a saline solution. I quickly lowered the dish to the bottom of the little apparatus filled with purified air. Whilst a current of purified air was passing through the apparatus I poured into it, by means of a small recently-heated platinum funnel, enough distilled hydrochloric acid to convert the oxide of calcium into chloride, to make the solution decidedly acid, and to raise the liquid to the top of the hollow cone. I then put into the top of the apparatus the pure rubber plug, fitted with its pointed platinum rod which had been washed and heated to redness at the same time as the funnel.

Having caused air, which had been purified and saturated with moisture, to circulate in the apparatus, I stopped the current by closing the taps in the tube. By using the direct-vision spectroscopy by M. Hilger, and the Steinheil spectroscopy, I analysed an induction spark without a condenser, flashing from the top of the platinum cone covered with the calcium solution; towards the point of the platinum rod, which was from 2 to 4 m.m. long, I noticed that the *sodium D line was entirely absent* from the spectrum. This consisted entirely of either the electric spectrum of calcium, or of this spectrum together with Fraunhofer's hydrogen C line, or, simultaneously,

the electric spectrum of calcium, the red hydrogen line and some air lines, according to the length of the spark and the intensity of the electric discharge.

Having replaced the air in the apparatus by pure hydrogen, I found that the sodium line was still absent from the spectrum. Besides the electric spectrum of calcium, M. Rommelaere and I always saw the red hydrogen line, but we tried in vain to see Fraunhofer's F, G, and H hydrogen lines.

Having found, by spectroscopic observations, that the air of the large room I was working in was comparatively pure, I withdrew from the above-mentioned apparatus the small platinum dish with the liquid calcium salt, and immediately put some of the liquid into pure hydrogen burning in air, by means of a recently heated platinum spiral. Spectrum analysis of the blowpipe, thus charged with calcium, showed the *flame spectrum* of chloride of calcium, *entirely* free from the sodium line. I repeated the experiment several times, and always with the same result.

I carried a small water-bath, heated by a Bunsen burner, into the large room devoted to spectroscopic work, and I put on this bath the small platinum dish containing the hydrochloric solution of chloride of calcium. Whilst it was being evaporated, I analysed the calcium liquid, at intervals of ten minutes, by introducing portions of it into a burning hydrogen blowpipe by means of a platinum spiral. As the air of the room was being more and more charged with sodium, owing to the presence of several people for more than an hour, I judged it necessary to provide a means of comparison during the analysis. For this purpose I arranged a second hydrogen blowpipe as near as possible to the prism, in such a way that the spectra of the two flames were as accurately as possible superposed. By doing this, I found that the solution became more and more charged with sodium as it evaporated; and long before it was so concentrated as to solidify on the spiral when cold, the sodium line was seen to be brighter than that in chloride of calcium made and fused in contact with the surrounding air.

I tried to verify the above results by substituting an acid solution of nitrate for the hydrochloric solution of chloride of calcium. For this purpose, I made this solution of oxide of calcium free from sodium, and a 10 per cent solution of nitric acid, distilled, collected, and kept in platinum, working in exactly the same manner as I did when making the hydrochloric solution of the chloride. I thus found that the acid solution of nitrate of calcium, when put into a spark or flame, showed, on spectrum analysis, a spectrum quite free from the yellow sodium line, and that the solution, when evaporated on a bath in the surrounding air, collected sodium from the air in the same way as the hydrochloric solution of chloride of calcium.

Thus it is proved, beyond a doubt, that the presence of sodium in the flame and electric spectra of chloride and nitrate of calcium, made from pure elements, but in contact with the surrounding air, is due to the occlusion of sodium present in the air.

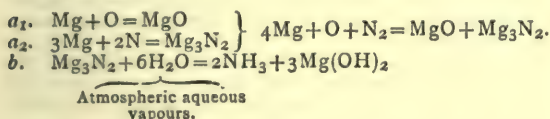
(To be continued).

The British Adulteration Laws.—(*Chem. Zeitung*).—The annual report of Dr. Sedgwick Saunders, the Public Analyst for the City of London, discusses the position of British analysts under the "Food and Drugs Adulteration Act." The hopes of an alteration and an improvement in legislation are still unfulfilled. The official chemists of Somerset House are still empowered to criticise and reject any analysis, even if it has been obtained from the most eminent analysts, and the decisions of many Courts throughout the country are still in flat defiance not merely to Science, but to practical common sense. The report of the Special Parliamentary Committee on this subject, in spite of its bulk, leaves much to be desired as regards the thoroughness of investigation,

COMBINATION OF ATMOSPHERIC AND CHEMICAL NITROGEN WITH METALS.

By P. L. ASLANOGLU.

PERHAPS it will be remembered that I published an article in the CHEMICAL NEWS of August 29, 1890 (vol. lxii, p. 99), entitled "Ammonia formed by Burning Metallic Magnesium in Contact with Atmospheric Air," and in which I pointed out the possibility of the estimation of the composition of the atmosphere by these means. In it I gave approximately the formulæ of the reactions, viz.,—



In communicating to the CHEMICAL NEWS the above fact, I did not state then any quantitative results; it was merely published as a notice. By further experiments in the same year, I found that the ammonia formed during the combustion of metallic magnesium in the open air was the following:—

The resulting substance was of a dirty grey greenish yellowish colour (a colour rather difficult to define), smelling strongly of ammonia. When acted upon by water it rose in temperature considerably, and if handled with slightly moist hands it felt hot and irritating to the skin.

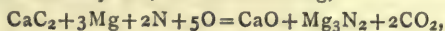
100 grms. of this substance, $2\text{NH}_3 + 3\text{Mg}(\text{OH})_2$, gave 15.438 grms. of ammonia, equal to 12.7 nitrogen, which if calculated on Mg_3N_2 minus the six atoms of water (atmospheric aqueous vapour), will give 26.416 nitrogen as percentage, the molecular weight of Mg_3N_2 being 100; therefore, by my method, I found that 26.416 per cent of nitrogen is taken from the atmosphere, the theoretical amount of nitrogen in Mg_3N_2 being 28 per cent as against 26.416 per cent found by my experiments.

	Per cent.
Theory	28
Found	26.416
Difference (in deficiency)	1.584

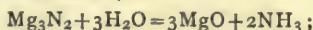
This reaction leads to the formula—



In an article entitled "Direct Combination of the Nitrogen of the Atmosphere with Metals in the State of Magnesium, Aluminium, Iron, Copper, &c., Nitrides," by A. Rossel, which appeared in the CHEMICAL NEWS (vol. lxxiii, p. 62), the author seems to have obtained a nitride of magnesium by heating the metal with calcium carbide, and to have found that 23 per cent of nitrogen is taken from the atmosphere, his formula being,—



and when acted upon by water ammonia was given off according to his formula,—



he found 23 per cent N, as against 28 per cent demanded by theory.

	Per cent.
Theory	28
A. Rossel's experiments	23
Difference (in deficiency)	5

Which is further removed from the theory than what I found by 3.416 per cent.

But, as you will see by my above formula (a_1), the magnesium first burnt with the oxygen resulted in magnesium oxide, and then an additional magnesium burnt,

so to speak, with the nitrogen formed magnesium nitride, as per formula a_2 ; but the presence of atmospheric aqueous vapours acting at the same time on the magnesium nitride formed ammonia and magnesium hydrate, as per formula b . Thus, the resulting substance of my experiments was nothing more than a mixture of ammonia and magnesium hydrate.

But what becomes of the aqueous vapours of the atmosphere in the experiments of A. Rossel?

I have obtained magnesium nitride in a yellow form by the following method, giving 26.82 per cent of nitrogen, and corresponding to the formula Mg_3N_2 , and higher than that of A. Rossel's experiments.

	Per cent.
Obtained	26.82
A. Rossel's experiments	23
Difference less from my expts.	3.82

I must mention here that Professor W. Ramsay's magnesium nitride in his work with argon finds 26.1 per cent nitrogen taken from the atmosphere (*vide* CHEMICAL NEWS, vol. lxxi, p. 52). Therefore the percentage of nitrogen taken from the atmosphere in the form of magnesium nitride is:—

Identical methods.		
Calcium carbide method.		
Prof. W. Ramsay's, 1894.	A. Rossel's, 1896.	P. L. Aslanoglou's, 1890.
Per cent.	Per cent.	Per cent.
26.1	23	1st meth., 26.416
		2nd meth., 26.82
		Chemical nitrogen.
		3rd meth., 27.213
	Theory, 28	
	Difference (in deficiency), 1.9	(1) 1.584
		(2) 1.18
		Chemical nitrogen.
		(3) 0.787

Second Method.—A quantity of metallic magnesium powder was well dried at 100° C. for several hours, and air was slowly bubbled through a series of tubes:—

1. Three tubes concentrated sulphuric acid;
2. Three tubes caustic potash;
3. Three tubes alkaline pyrogallate;
4. Three tubes fused calcium chloride;
5. Three tubes soda-lime;

and condensed into a long combustion tube containing the dried metallic magnesium in powder. After time had been allowed to expel all air from the whole apparatus, the magnesium was heated, and any gases unacted upon were cooled by a direct condenser (Graham's) and received in a vacuum tube with magnesium electrodes. When the action was finished, the vacuum tube was sparked through, and I distinguished the nitrogen spectrum, but some time after the nitrogen acted on the magnesium electrodes, attacking at the same time the glass and leaving a fine yellowish film on the sides of the tube; eventually the nitrogen spectrum disappeared, giving only a bluish fluorescence.

Third Method.—By ammonia gas, otherwise chemical nitrogen. The plan adopted was similar to the second method, except the absorption tubes, which were in series of six tubes caustic potash and six tubes lime.

The vacuum tube was sparked through when I distinguished the hydrogen spectrum. This sample of magnesium nitride was of a lighter colour than that found in the second method, and gave 27.213 per cent nitrogen, as against theory 28 per cent.

	Per cent.
Theory	28
Found	27.213
Difference (in deficiency)	0.787

I have tried metallic copper, iron, zinc, aluminium, and clay in fine powder, strongly heating them in the open air, but I failed with the first three; while aluminium gave a somewhat similar reaction to magnesium, but not distinctly enough to encourage me to pursue my researches by this method, or it may be due to the temperature not being high enough. Clay, when strongly heated, gave an ammonia smell which soon disappeared. I have often noticed, in smoking tobacco in a clay or meerschaum pipe, an ammoniacal smell. Is this due to results as above, or to the N_2 of nicotine, $(C_5H_7)_2N_2$? And when a fairly old clay or meerschaum pipe is heated by a Bunsen burner there occurs a most violent explosion, shattering it into atoms. I have followed up my investigations on atmospheric and chemical nitrogen since 1890 in the form of nitrides, and I must say that nitrogen is a difficult agent to work with, and here is another instance which was published by me in the *CHEMICAL NEWS*, vol. lxiv., p. 313), "The Supposed Copper Nitride." In the *Phil. Mag.*, 3, xix., 100, July-Dec., 1841, Mr. W. R. Grove, M.A., F.R.S., refers to some electrolytical experiments in which, when a piece of metallic copper is connected with the positive pole and the negative pole of a battery with a platinum plate in a solution of ammonium chloride, copper nitride was formed. But on repeating his experiment several times I found that no copper nitride is formed, but only a mixture of copper oxide with metallic copper, corresponding to the formula $Cu_2O + Cu$. And in the same volume of the *Phil. Mag.* (p. 102) Mr. W. R. Grove says it may be worth remarking that the quantities of nitrogen which enter into combination with the metals are in proportion to their affinity for oxygen, and it may perhaps be considered an argument in addition to the many already advanced to prove that nitrogen is an oxide.

A. Rossel gives us only the percentage of nitrogen taken from the atmosphere in the case of magnesium, although he has obtained nitrides of aluminium, iron, copper, &c. It would be interesting to know the percentage of nitrogen which enters into combination with these metals.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 28th, 1896.

Prof. JOHN PERRY, Vice-President, in the Chair.

SIR D. SALOMONS showed some Experiments with Incandescent Lamps.

A large electro-magnet is excited by means of a continuous current, while an alternating current is passed through an incandescent lamp. On bringing the lamp near the magnet the filament is set in vibration, which, if the lamp is brought sufficiently near the magnet, is sufficiently intense to break the filament. The number and position of the nodes formed in the vibrating filament are found to be independent of the natural period of the filament, but depend on the frequency of the alternating current.

Prof. S. P. THOMPSON asked whether it was not found that the number of segments into which the filament is divided depend to some extent on the natural period of the filament.

Prof. AYRTON said that the magnetic leakage was very large with the arrangement adopted, and he would like to know whether this method was a more sensitive one for mapping out the field than those ordinarily employed. In an instrument designed by Prof. Perry and himself, an alternating current was passed through a wire stretched between the poles of a magnet, and the tension of the wire was altered till the vibrations set up were a maxi-

mum. The natural period of the wire, and hence the frequency of the alternating current, was then deduced from the tension, &c. In Prof. Ewing's magnetic curve tracer, on the other hand, the natural period of the stretched wire was made as different as possible from the period of the alternations which were to be observed, so that the natural vibrations of the wire did not influence the result. The author's arrangement appeared to him (Prof. Ayrton) to be intermediate between these two, and it would seem that the natural period of the filament would, to a certain extent, influence these results.

Prof. PERRY suggested that the lamp might be held in a very steady support, so that after the large vibrations due to the natural period of the filament had died out, the vibrations of the period of the alternations alone could be observed.

SIR D. SALOMONS, in his reply, said that the arrangement was not intended for making measurements. A lamp had been fixed in a steady clamp and the current passed for many hours, but the character of the vibrations remained unaltered. He had found the vibrating filament useful for microscopic work where any surface rather than a line of light was required.

Prof. FLEMING read a paper, by himself and Mr. PETAVEL, on "An Analytical Study of the Alternating Current Arc."

The first part of the paper consists of an analytical study of the distribution of light throughout the various radiating regions in the arc when supplied with electric power of known constant amount, the periodic variations of the current through the arc, and of the potential difference between the carbons being at the same time recorded. The power was measured by means of a bifilar watt-meter; while, by means of a series of mirrors and a rotating disc carried by a synchronising alternating current motor, the mean value of the light taken from any part of the arc was compared with the instantaneous value of the light taken from the same part of the arc, and taken at any assigned instant during the period. Thus, the arc itself was its own standard, and difficulties due to slow variations in the mean light of the arc disappear.

The facts observed may be summed up as follows:—The purple light of the true arc undergoes a periodic variation, and, as far as the eye can judge, is completely extinguished during a certain interval during the phase; it has equal maxima values during the period, at instants slightly lagging behind the instants of maximum power expenditure in the arc. On the other hand, the illuminating power of the carbon crater varies between a minimum value and two unequal maxima; the greater maximum occurring when the carbon is positive and at an instant slightly lagging behind the instant of maximum power expenditure in the arc. The second part of the paper consists of a comparison of the efficiency of the alternate current arc regarded as a light-giving agent, as compared with that of a continuous current arc, taking the same mean power. Using two arcs which may be regarded as typical of those used in practice, the mean spherical candle-power was compared for equal expenditure of power in the arcs; and it was found that, for the alternating current arc employed, the total mean spherical candle-power was always less than that of the continuous current arc. Lowering the frequency seems to decrease the efficiency of the alternating current arc.

Prof. AYRTON said the behaviour of the alternate current arc was of great interest, for the power supplied could not be measured by simply multiplying the current by the electromotive force, since the current lags behind the volts. The resistance, i.e., the ratio of the current to the E.M.F., also lags, but the authors do not appear to have made any attempt to measure the true resistance. The authors were to be congratulated on the guarded tone they had adopted as to the bearing of these experiments on the question of the relative efficiency of the alternating and continuous current arcs. In a previous communica-

tion, one of the authors had stated that the alternating current arc must necessarily be a less efficient light-producing agent than the continuous current arc. Although the last set of curves given in the paper might appear to support this supposition, he (Prof. Ayrton) felt that the difference obtained was probably due to the fact that the alternating current arc was not being worked under proper conditions. The quality of the carbons and the length of the arc have a most important influence on the efficiency of an arc. At present, our knowledge is not sufficient to allow of our stating definitely whether or not an alternating current arc can be made as efficient as a direct current arc, but there is no doubt that it will be possible to get much better results than are at present attainable.

Prof. S. P. THOMPSON said that when the fact of the existence of the difference in phase between the current and volts in an alternating arc was first published, he made some experiments which showed that there was a lag, and not a lead, *i.e.*, that the arc acted as if it possessed self-induction. The resistance also lagged, and he thought this lag might be due to a thermal lag. The temperature of the arc will lag behind current, both when it is increasing and when it is decreasing, and if the resistance of the arc depends on the temperature of the vapour in the arc, then the resistance would also lag behind the current. It was not possible from *a priori* reasoning to say whether or no an alternating current arc could ever be obtained of an efficiency equal to that of the direct current arc. With suitable carbons, length of arc, current, and volts, it seemed to him that it might be possible to obtain an equal efficiency. The light-giving process in an arc is not merely an irreversible degradation of electric energy into heat; for the difference of potential between the carbons may be written $V = a + bl$; where a may be regarded as a back electromotive force, and bl as a true resistance. The first term of this expression does not vary with the length of the arc (l), but the second term does. Multiplying through by the current (C), the equation—

$$\text{Watts expended} = Ca + Cbl$$

is obtained. It is the first of the terms on the right-hand side, which is a reversible effect, and corresponds to the power expended in driving the current against a back electromotive force, on which the light given out chiefly depends, due to something occurring at the crater surface.

Mr. BLAKESLEY asked whether Prof. Thompson's idea of the light being due to the reversible part of the process was not a strong argument in favour of the direct current arc.

Prof. AYRTON said that in two communications made to the Congress held at Chicago it was shown that even with direct-current arcs there was a certain length of arc for which the efficiency was a maximum. Mrs. Ayrton had quite recently found that the efficiency of arc lamp carbons altered with time. Prof. Thompson's suggestion as to a thermic lag was a valuable one.

Prof. FLEMING, in his reply, said that when comparing two agents where there were so many variables, it was practically necessary to restrict the investigation. In their case they had kept the mean power constant and had left the other variables to take care of themselves.

The Society then adjourned till March 13th.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Fifth Ordinary Meeting, January 27th, 1896.

DR. DOBBIN read a paper on "Scheele as a Chemist."

This paper, which is incapable of abstraction, was a discussion of Scheele's paper on the "Colouring Principle of Prussian Blue."

Sixth Ordinary Meeting, February 10, 1896.

Mr. W. W. TAYLOR, M.A., read a paper on "Chemical Theories."

Seventh Ordinary Meeting, February 24th, 1895.

Dr. J. E. MACKENZIE read a paper on the "Metallurgy and Analysis of Copper," of which the following is an abstract.

Native copper is found in large quantities, notably near Lake Superior. The chief difficulty of working it is its occurrence in immense masses, these having to be cut through by chisel in order to be made portable.

The treatment of copper ores may be divided into three classes:—

- I. Of ores free from sulphur.
- II. Of ores containing sulphur.
- III. Of ores containing very small percentages of copper (3 per cent and under).

I. The minerals so worked are cuprite, malachite, and azurite. The two latter are found in large quantities in the Ural mountains; the finer varieties being used as ornamental stones. The metal is won from these ores by fusion with charcoal in a small blast furnace; the impure metal being refined by melting in a small furnace with hemispherical bed, a blast of air being directed on to the metal to oxidise the impurities.

II. The minerals here treated are copper pyrites (or chalcopyrite), bornite (or purple copper ore), copper glance (or redruthite), and indigo-copper; the first-mentioned being that most commonly used. The ores first undergo calcination in heaps, "stalls," kilns, or reverberatory furnaces.

The first two methods are somewhat wasteful, and only adopted where timber is abundant. Kilns are generally used for ores poor in sulphur. In the Swansea district reverberatory furnaces are mostly used. The temperature of the furnace is not raised so high that the ore fuses. In calcination, most of the As and part of the sulphur are converted into oxides, and carried off with the products of combustion. The calcined ore now undergoes the "melting" or "fusion" process, after mixing with "metal slag." The resulting product, known as "coarse metal," is granulated by running into water. It should approximate to the formula CuFeS_2 . The granulated metal is again roasted, the iron sulphide being converted into oxide. The "roasted coarse metal" is now fused with refinery slags, so that the iron is carried off in the slag as a silicate, and the copper separates as "white" or "fine metal." This should contain about 75 per cent Cu, and nearly correspond to the formula Cu_2S . It is then roasted; by which process sufficient Cu_2S is converted into Cu_2O , so that when melted they may react and form Cu and SO_2 . On fusion the reaction takes place with violent boiling. The crude copper is known as "blister" or "pimple copper" from its appearance, and it should contain about 95 per cent Cu. It is refined by melting and oxidation of the impurities, and then "poling" to reduce the copper which had been oxidised.

III. Burnt pyrites from sulphuric acid works frequently contain small amounts of copper. They are calcined with rock salt, by which means copper chloride is produced. By scrap iron, the copper is precipitated from its solution. The crude copper is purified as above, or by electrolysis. Certain ores, on treatment with dilute sulphuric acid, give up their copper as sulphate, which, in its turn, may be treated with scrap iron.

The ordinary methods of analysis were briefly mentioned, special emphasis being laid on the electrolytic.

Photographs obtained with the Röntgen Rays.—A. Isbert and H. Bertin Sans.—An account of certain photographs of diseased portions of the internal parts of the human system. No new principle is brought to light. —*Comptes Rendus*, cxxii., p. 384.

NOTICES OF BOOKS.

Practical Studies in Fermentation, being Contributions to the Life-History of Micro-Organisms. By EMIL CHR. HANSEN, Ph.D., Professor and Director at the Carlsberg Physiological Laboratory, Copenhagen. Translated by ALEX. K. MILLER, Ph.D., F.I.C., F.C.S., and Revised by the Author. London: E. and F. N. Spon, 125, Strand. New York: Spon and Chamberlain, Cortlandt St. 1896. 8vo., pp. 277.

WITHIN the recollection of persons still living, brewing was perhaps the very type of a rule-of-thumb trade. Experience and care in the selection of his materials often enabled the brewer to obtain satisfactory results, but he was always at the mercy of accidents. A variation in the quality of the water employed, of atmospheric influences, of the malt, and above all of the yeast, might at any time involve a failure as inexplicable as disastrous.

More correct views, involving a reform in practice, were initiated by Cagniard Latour, Schwann, Turpin, and Kützing. The nature of fermentation was scrutinised, and, in opposition to the view of Liebig, it was shown to be essentially a biological process. The high philosophic import of this result has made itself widely felt. It has thus been shown, in opposition to Comte and others, that the so-called simpler sciences cannot be constituted without the aid of those more complicated. In this task Pasteur took a most important part. It was shown to be a capital precaution that the yeasts employed should be "pure," *i. e.*, free from the "wild yeasts" which set up so-called diseases in beer, and render it unsaleable. But how is the pure yeast to be regularly and constantly obtained? Pasteur's method—the addition of a solution of cane-sugar to which tartaric acid had been added—certainly suppressed the bacteria present in the yeast, but it proved unsuitable for the production of a good brewery yeast.

Our author shows that of the *Saccharomycetes* known, one species only gives a normal beer of a good flavour and odour. The species which he recommends is that now widely known as "Carlsberg bottom yeast, No. 1."

The disappointment experienced in breweries, and the occurrence of diseases in beer, are traced to the presence of foreign species which have gained entrance. The most dreaded of these intruders is *Sacch. Pasterianus* L., which gives a peculiarly unpleasant taste and disagreeable odour. A single species of yeast is able to effect the entire fermentation, and special secondary yeasts are not necessary. This has been fully proved in German breweries, both for top and bottom fermentation.

It must not be supposed that the activity of ferment-microbia is confined to beer. Leaving out of question wines, ciders, and fruit wines, all of which may be much improved by careful attention to the processes of fermentation which they undergo, and to the improvement which they may receive by the use of a pure and suitable yeast, we find that butters and cheeses, if to be of the best quality, must receive ferments of a faultless quality. Many German dairies have been supplied from Weigmann's laboratory with pure cultures of a bacterium which is employed for souring cream.

The principle has been introduced in the tobacco manufacture. According to Suchsland, of Halle, the ordinary tobacco can, by means of fermentation, be made to acquire a superior aroma, a change for which there was some little room.

In the preservation of vinegar we must not omit to mention that it is much improved by the application of heat—of course in an air-tight vessel. This method of treatment was devised by Scheele as early as 1782.

How long will it be before we discover all the merit of the unobtrusive Swedish chemist?

Pure yeasts are also advantageously employed in the manufacture of bread.

This work should be carefully studied by all persons who are concerned with fermentation processes.

Cyanide Processes. By E. B. WILSON, E.M. New York: John Wiley and Sons. London: Chapman and Hall (Ltd.). 1896.

COSTLY litigation has of late attracted no little attention to improved means of extracting gold from auriferous quartz, tailings, &c. Among such methods the cyanide process, in its various modifications, of course takes the lead. The author disclaims any attempt to criticise the mechanical arrangements for the process, as they must vary with local circumstances. He admits that, as early as 1806, the solubility of gold was mentioned by Hagen. But he holds that "it is of no special moment to us who discovered the process, or whose process or patent is valid; that McArthur's people proved the way by practical demonstration is of more value to the world than who owns the patent." Yet he points out that McArthur at first pronounced the intervention of oxygen in the process unnecessary, but afterwards repented. The credit of first applying electricity is given to Siemens and Halske, and the author insinuates that McArthur was afraid of the Siemens and Halske process when he accused the electric current of dissolving the base metals (p. 103). He asserts (p. 73) that neither McArthur and Forest nor Siemens and Halske "designed or produced anything new, but, having strength in their convictions, they applied their patents to obtain useful results." But, in addition to strength in their convictions, they had at their disposal the needful funds. Many inventors may have strong convictions, but cannot obtain the capital for their applications on a useful scale. The author holds that Siemens and Halske made two great improvements over the old process, *viz.*, saving cyanide and zinc and trouble in refining.

Mr. J. B. Hannay's process (Hannay?) is pronounced an admirable plan to obtain all the good points. It is said to yield an average of 86.1 per cent.

The process of W. Crookes (Patent 462,535; 1891) is described at some length, with the comment that "it may be successful in the laboratory on rich ores, but we have never heard of it beyond the patent specification."

Apparently all the cyanide processes are described, but we do not see that a decided preference is ascribed to any. The index might with great advantage have been made more copious.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 6, February 10, 1896.

At this meeting of the Academy the President announced the death of Jules Reiset, a member of the section on Rural Economy.

Study of Uranium Carbide.—Henri Moissan.—To obtain this compound, the author takes 500 grms. of the green uranium oxide mixed with 60 grms. sugar charcoal, both in fine powder, and heats 800 grms. of this mixture, contained in a crucible of coke, in the electric furnace for eight to ten minutes, using a current of 900 ampères and 50 volts. In about five minutes the reaction is produced with an issue of electric sparks. The liquid carbon is allowed to solidify and cool in the furnace. It has a crystalline fracture. Its specific gravity, taken in benzene, at 18° is 11.28. It scratches rock crystal, but not corundum.

If pulverised without precautions, it takes fire. If slightly heated it is attacked by fluorine. At 350° it is attacked by chlorine, and at 390° by bromine. Hydrochloric, sulphuric, and nitric acids attack it slowly in the cold. Its composition corresponds to the formula C_3O_4 . Its behaviour with water enables us to obtain hydrogen carbides, both gaseous, liquid, and solid.

Action of Currents of High Frequency upon Bacterian Toxines.—MM. d'Arsonval and Charrin.—Experiments proved that currents of high frequency attenuate the bacterian toxines. Toxines thus attenuated increase the resistance of animals into which they have been injected.

Application of the Rays of Röntgen to Surgical Diagnosis.—MM. Lannelongue and Oudin.—Already inserted.

Campholide: a Product of the Reduction of Camphoric Anhydride.—A. Haller.—This substance has the composition $C_{10}H_{16}O_2$. It is formed by reducing with sodium amalgam an alcoholic solution of camphoric anhydride, keeping the liquid acid by means of dilute sulphuric acid.

Influence of the Chemical Nature of Substances on their Permeability by the Rays of Röntgen.—Maurice Meslans.—Already inserted.

Application of Röntgen's Method.—Albert Londe.—Already inserted.

Increase of the Photographic Yield of the Röntgen Rays by means of Phosphorescent Zinc Sulphide.—Charles Henry.—Already inserted.

Photographic Proofs obtained by means of X Rays.—Ch. V. Zenger.—Already inserted.

Mechanical Action emanating from Crookes Tubes analogous to the Photographic Action Discovered by Röntgen.—MM. Gossart and Chevalier.—Already inserted.

Copper Silicide.—M. Vigouroux.—Copper silicide is a very hard brittle substance, of a steel-grey, if recently fractured, but gradually assuming a reddish aspect. Its specific gravity at 18° is 6.9. Its composition is represented by the formula $SiCu_2$.

Thionyl Chlorobromide and Bromide.—A. Besson.—This paper is not adapted for useful abstraction.

Crystalline Tin Sulphophosphide.—A. Granger.—A blackish grey substance, insoluble in hydrochloric and nitric acids, and in aqua regia. When in a fine powder it dissolves readily in a solution of potassa or soda through which a current of chlorine or bromine is being passed.

Zinc Oxyiodides.—M. Tassily.—The author describes three of these compounds:— $ZnI_2 \cdot 9ZnO \cdot 24H_2O$, $ZnI_2 \cdot 5ZnO \cdot 11H_2O$, and $3ZnI_2 \cdot 5NH_3 \cdot 3H_2O$.

Determination of the Purity of Butter by means of its Specific Gravity.—Raoul Brullé.—The author shows the necessity of eliminating all water by means of appropriate desiccating agents, simple fusion being insufficient, as well as the colouring-matters and the caseine.

No. 7, February 17, 1896.

Preparation and Properties of Cerium Carbide.—Henri Moissan.

Lithium Carbides.—Henri Moissan.—These two memoirs will be inserted in full as early as possible.

Lowering of the Explosive Potentials, Static and Dynamic, by the X Rays.—R. Swyngedauw.—(See p. 109).

Electrical Phenomena produced by Röntgen's Rays.—A. Righi.—(See p. 109).

Action of Röntgen's Rays on Electrostatic Rays, and the Striking Distance.—J. J. Borgman and A. L. Gerchun.—(See p. 110).

Photographic Researches on the X Rays.—Auguste and Louis Lemièrre.—This paper will be inserted *in extenso*.

Experiments showing that the X Rays emanate from the Anode.—M. de Heen.—In order to take date, I have the honour to bring to your knowledge that, according to my last experiments, the X rays of Lenard and Röntgen emanate, not from the kathode, but from the anode. To demonstrate this, it is sufficient to place between the Crookes tube and the sensitive plate a screen of lead pierced with some apertures permitting the passage of bundles of rays. The direction of these on the plate shows that they emanate from the positive and not from the negative pole. They are therefore *anodic* rays.

Photographic Proofs obtained in Darkness.—A. Besançon.—I have the honour of submitting to the Academy two photographic proofs obtained under the following circumstances:—On the glass of a frame for positives I applied a leaf of black cardboard, covering it completely. Upon this leaf I arranged two sensitive plates, above which I placed a twig of cypress and a fish put up in a sheet of black cardboard; above all, a bed of blotting-paper. Then I closed the frame with its lid. The whole was wrapped up in several thicknesses of black cloth. These operations were performed in the camera. I then deposited the packet in a box hermetically closed in a room well closed. I had thus darkness as complete as possible. Two hours afterwards, I developed the proofs, and obtained the result which may now be seen. In my idea, this experiment was intended to verify a hypothesis which would explain the transmission of light through opaque bodies. All substances allow themselves to be saturated with the luminous rays; when once saturated, they give off the light which they have received, and can thus act in darkness upon a sensitive plate. The result of my experiment does not seem to fully confirm this hypothesis; for the negative image of the object, instead of being light, ought to be black. Perhaps further experiments may give the explanation of this apparent anomaly. However this may be, a body which has been exposed to light impresses a sensitive plate in darkness.

Rapid Process for the Determination of Arsenic.—R. Engel and J. Bernard.—This paper will be inserted in full.

Practical Synthesis of Geranic Acid. Constitution of Lemonol and Lemonal.—P. Barbier and L. Bouveault.—This partial synthesis of geranic acid distinctly shows the accuracy of Tiemann's formula. This modification of the formulæ of lemonol and lemonal involves likewise the modification of those which we have proposed for licareol and licarhodol.

Certain Derivatives of Eugenol.—Ch. Gassmann.—An account of eugenolacetic acid, of isoeugenolacetic acid, and of vanilline acetic acid.

Composition of Fire-damp.—Th. Schloësing, jun.—We may generally, in practice, regard the combustible portion of fire-damp as consisting simply of methane. It may, however, comprise a proportion—small, but appreciable—of the hydrocarbons.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., Sir James Crichton-Browne presiding. The following were elected Members:—H. J. Allcroft, R. L. Andrews, Dr. Ernest Clarke, F.R.C.S., Mayo Collier, F.R.C.S., H. E. Fry, Mrs. Francis Gaskell, E. Gimingham, A. Glegg, Sir Cameron Gull, Bart., M.P., Miss Catherine Imray, C. W. Keighley, Dr. Edward Law, M.R.C.S., C. Letts, M. Micholls, R. E. Middleton, M.Inst.C.E., Dr. A. Paine, G. H. Sykes, M.Inst.C.E., and W. L. Wise, J.P.

The City and Guilds of London Institute.—The Executive Committee have awarded the second Salters' Company's Research Fellowship for the encouragement of Higher Research in Chemistry in its relation to Manufactures to Sidney Williamson, Ph.D., F.I.C., F.C.S., who was for two years a student at the City and Guilds Technical College, Finsbury, and subsequently for three years at the City and Guilds Central Technical College. The Fellowship is tenable at the latter, and Dr. Williamson proposes to work on some questions bearing on food-stuffs generally, more particularly the examination of some definite albumenoids, with the ultimate object of ascertaining the influence of various manures on the growth of crops in so far as *quality* of produce is concerned.

MEETINGS FOR THE WEEK.

MONDAY, 9th.—Medical, 8.30.
TUESDAY, 10th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.
— Society of Arts, 8. "English Book Illustration, 1860—70," by Joseph Pennell.
— Medical and Chirurgical, 8.30.
— Photographic, 8.
— Institute of Civil Engineers, 8.
WEDNESDAY, 11th.—Society of Arts, 8. "Peasant Life and Industries in Ireland," by Prof. A. C. Haddon.
— Geological, 8.
— Pharmaceutical, 8.30.
THURSDAY, 12th.—Royal, 4.30.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Masters of Modern Thought—II. Rousseau," by The Rev. W. Barry, D.D.
FRIDAY, 13th.—Royal Institution, 9. "The Theory of the Ludicrous," by W. S. Lilly, M.A.
— Physical, 5. "An Addition to the Wheatstone Bridge for the Determination of Low Resistances," by J. H. Reeves. "On Kathode Rays," by Herr Paley.
— Astronomical, 8.
SATURDAY, 14th.—Royal Institution, 3. "Light," by Lord Rayleigh, F.R.S., &c.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1894.

ON THE ACTION OF THE X RAYS UPON THE DIAMOND.

By ABEL BUGUET and ALBERT GASCARD.

THE transparency of the different varieties of carbon and of its non-metallic compounds, established by Professor Röntgen and then by the experimentalists who have studied the X rays, may serve to distinguish clearly the diamond from its imitations made of very opaque substances.

The proofs which we have the honour to submit to the Academy show in juxtaposition silhouettes of genuine diamonds and of imitations both loose and set. Prolonged exposure soon succeeds in causing the silhouettes of genuine diamonds to disappear, whilst false diamonds continue to behave like opaque substances. The same procedure has also allowed us to distinguish natural jet from its mineral imitation.

In addition to this graphic method we have tried an optical method, in which we have tried the fluorescence studied by Prof. Röntgen. Diamond and jet, if interposed between the Crookes tube and a leaf of paper covered with a fluorescent substance (e.g., barium platino-cyanide), project upon the paper shadows lighter than those which appear beneath imitations placed near.

Here then we have two very certain tests: the graphic method leaves an irrefutable document, whilst the optical method is instantaneous. They will easily come into practical use, since a precious stone may be tested even in its setting, and without running any risk.—*Comptes Rendus*, cxxii., p. 457.

ON CERTAIN PROPERTIES OF DARK LIGHT.

By GUSTAVE LE BON.

DARK light seems, as I have indicated, to consist of a spectrum of very different rays, whence the term dark light must be considered as applicable to all the radiations invisible to the eye, but visible to the photographic plate or to any instrument.

Organic substances are generally easily traversed by the cathodic rays, and very badly by dark light. Hence we can only photograph the bones with the cathodic rays, since all the other parts are as transparent to these rays as crystal is to solar light.

As dark light traverses organised substances unequally and with difficulty, we may perhaps succeed in photographing the various layers of certain tissues. I have the honour of submitting to the Academy photographs of frogs taken with dark light. They still show only the more superficial parts of the animal. They have been taken in an ordinary frame between a polished copper plate and a sheet of lead, the whole exposed to the light of day. The interposition of a plate of glass between the sensitive surface and the animal does not prevent the formation of the image, but causes it to lose much of its distinctness, as would be the case with the reproduction of any proof.

I will add, according to my most recent researches, that certain organised beings appear to have the property of emitting, in dark places, radiations of dark light capable of acting on photographic plates. I submit to the Academy the photograph of a frog produced in complete darkness, merely by placing it for two hours on a sensitive plate in a frame. The parts reproduced differ,

however, from those obtained in the foregoing experiment.

Not all organised bodies can be thus reproduced. The living human hand, exposed for an hour and a half upon a sensitive plate in darkness, gives no trace of an image if it has been perfectly cleansed.

It might be objected, to the experiment of the reproduction of the frog in darkness, that the reduction of the silver salts constituting the image is due to chemical compounds present in the viscid liquid with which the animal is coated, and, in fact, the interposition of a plate of glass between the sensitive plate and the body of the frog prevents the appearance of the image. But the image is still formed if the viscid matter is removed by steeping the animal for some hours in alcohol at 90°. I cannot therefore decide exactly upon the interpretation of the results of this experiment.

There does not seem to exist any analogy between the phenomena just described and those called condensed light. Numerous experiments have convinced me that the majority of bodies do not possess the property of acting upon sensitive plates in darkness.—*Comptes Rendus*, cxxii., p. 462.

ON A RAPID PROCEDURE FOR THE DETERMINATION OF ARSENIC.

By R. ENGEL and J. BERNARD.

THE determination of arsenic, especially when small quantities are concerned, presents difficulties and causes of uncertainty, and always requires a considerable time.

With a view to biological researches, A. Gautier (*Bull. de la Soc. Chim.*, xxiv., p. 251) has studied the determination of arsenic by weighing the ring obtained by Marsh's method, and has carefully studied the conditions which must be observed to avoid any loss. This process, in the hands of the author and of one of his pupils, has given the most accurate results, but its application is very delicate, and its duration is rather long for ordinary determinations of arsenic.

The following procedure, disregarding the time of precipitation, requires only a few minutes, and gives very accurate results.

The principles on which it depends are as follows:—

1. The oxygen compounds of arsenic in solution in concentrated hydrochloric acid are entirely reduced by hypophosphorous acid to the state of non-metallic arsenical compound, as appears from the earlier experiments of one of us.
2. Iodine in solution transforms non-metallic arsenic (i.e., arsenic in combination with a non-metallic element) into arsenious acid, with the formation of merely small quantities of arsenic acid as long as the liquid remains acid. In a liquid rendered alkaline by bicarbonates the transformation into arsenic acid is total.

The procedure is carried out as follows:—

To an arsenical solution brought to 20 c.c. or 40 c.c. by concentration in an alkaline solution, if needful we add three times its volume of hydrochloric acid at sp. gr. 1.169, and then a large excess of hypophosphorous acid; according to the presumed quantity of arsenic, we use from 4 to 10 c.c. of a solution of this acid at 1.299 sp. gr. The precipitate at ordinary temperatures appears as a brown powder. It is well to operate in a vessel of the shape of a truncated cone, with a ground glass stopper.

After standing for about twelve hours, the mixture is gently heated in the water-bath. We add an equal volume of boiled water, still boiling: this operation is to facilitate the precipitation, which is more rapid with hot liquids.

The clear liquid is first filtered, and the precipitate is then brought upon the filter. We wash the vessel and

the precipitate with boiling water, without regarding a very slight deposit which sometimes adheres to the vessel. We wash until the filtrate is no longer acid. The filter containing the precipitate is then returned to the vessel in which the precipitation was effected, and we add gradually, from a graduated burette, a decinormal solution of iodine, with continual stirring. The first quantities of iodine are rapidly decolourised. As only three-fifths of the total iodine necessary to transform the arsenic into arsenic acid are consumed in dissolving the arsenic, we may, after each decolouration, add at once rather more than half the volume of iodine without risk of adding excess. It is essential not to add water at this stage of the operation, in order that the solution of iodine may remain sufficiently concentrated to react rapidly.

When after a last addition the liquid remains coloured, we wait two or three minutes, stirring from time to time, so as to dissolve the last traces of arsenic adhering to the filter or to the glass. We add then about 50 c.c. of water and 10 c.c. of a saturated solution of sodium bicarbonate. This addition determines the immediate decolouration of the liquid and of the fragments of the filter.

We complete the titration with iodine, using starch as indicator, as in the well-known titration of arsenious acid by iodine. Each c.c. of iodine employed corresponds to 0.0015 grm. of arsenic.

This determination may be effected in presence of all the metals of the third, fourth, and fifth groups.

Here follow the results of some analyses in which known quantities of arsenious acid have been added to saline solutions of the following metals:—

Metal along with arsenic.	Arsenic added.	Arsenic found.
Nickel	0.054	0.0539
Cobalt	0.074	0.0735
Manganese ..	0.050	0.0589
Aluminium ..	0.084	0.084
Zinc	0.123	0.1229

As 1 c.c. of decinormal solution of iodine corresponds to 1.5 m.grm. of arsenic, we see that it is possible, without an appreciable error, to determine 1/10th m.grm. with ordinary burettes.—*Comptes Rendus*, cxxiii., p. 390.

ON THE NATURE OF AN OXIDISING SUBSTANCE PRODUCED BY DISTILLING AQUEOUS SOLUTIONS OF POTASSIUM PERMANGANATE AND SULPHURIC ACID IN VACUO.

By COLIN C. FRYE.

SOME years ago, it was found by Dr. Collie that when solutions of sulphuric acid and potassium permanganate of certain strengths were distilled *in vacuo*, the distillate liberated iodine from potassium iodide. It is also given in some text-books that ozone can be prepared in this manner, and it was to prove this that this investigation was carried out.

The substance that liberated iodine might possibly have been any of the following:—Persulphuric acid, permanganic acid, peroxide of hydrogen, or ozone.

The first thing to do was to find out what strength of solution gave most of this substance, or liberated most iodine; and about thirty experiments were carried out for this purpose. Great care was taken to avoid splashing of any kind, as this, of course, would have vitiated the result.

A mean of 0.008602 grm. of iodine was liberated in these experiments. No iodine was liberated from solutions of under 22 per cent strength of both sulphuric acid and potassium permanganate. After this, iodine was

liberated up to 50 per cent strength of both solutions, above which strength large quantities of oxygen were evolved. The iodine-liberating agent in the distillate decomposes completely in about fifteen minutes.

For Peroxide of Hydrogen.—The distillate was mixed with a solution of sulphuric acid and potassium bichromate, and then shaken with ether. No blue colour was imparted to the ethereal layer, but it was afterwards found that this test does not work with solutions so dilute as this one might have been. Also, no peroxide of hydrogen could be detected by the extremely delicate titanous acid test recommended by Mr. A. Richardson (*Journ. Chem. Soc.*, 1893, p. 1110).

For Persulphuric Acid.—Sixteen distillations were made, and the collected distillates allowed to decompose and then precipitated with barium chloride, but only 0.001 grm. of barium sulphate was obtained; whereas, if it had been persulphuric acid, and had decomposed into sulphuric acid and water, one ought to have got about 0.3000 grm. of barium sulphate (calculated by the iodine liberated from each).

For Permanganic Acid, or a Manganese Compound.—The substance was distilled through a red-hot tube, and then conducted into a solution of potassium iodide. No iodine was liberated, and no deposit of any manganese compound was perceived on the cooler portion of the tube.

Ozone.—The distillate before condensation was passed through a warm tube containing manganese dioxide, when it did not liberate iodine; but when the manganese dioxide tube was omitted, it both liberated iodine from potassium iodide, and also had a slight action on mercury, when collected over it, oxygen being found.

From the above experiments it appears evident that the oxidising agent which is made by the action of sulphuric acid on potassium permanganate is ozone; but it is rather difficult to explain the fact that ozone should dissolve so readily in water, when the pressure is reduced to only about one-half to one inch of mercury; ozone prepared by sparking oxygen being very slightly soluble in water at ordinary pressures.

Chemical Laboratory, University College,
January 28, 1896.

THE DEPOSITION OF ALUMINIUM FROM AQUEOUS SOLUTIONS.

By H. N. WARREN, Research Analyst.

THE divers assertions put forth by various authors as regards the deposition of aluminium are not only fabulous, but in many cases alchemical.

In an exhaustive work on electrotype manipulation by Charles V. Walker, F.R.S., &c., the author claims to be able to produce aluminium from the decomposition afforded by the aid of three Smee's batteries; employing as a depositing solution, one obtained by incorporating pipe-clay with sulphuric acid. The same author further states that the metal may be readily detached from the electrode, if desired, as fast as deposited. Granting that this be both an inexpensive and at the same time ready method for the formation of that substance, how comes it that this method is not commercially employed?

During the past twelve months, various trials have been made at this laboratory with a view to ascertain the possibility of obtaining a deposit from aqueous solutions; and, among other methods, consisting in the decomposition of cyanides, sulphocyanides, sulphides, and various other aluminous compounds, was attempted the decomposition of kaolin, as before stated. In this case the writer also obtained the white deposit formerly referred to, but which upon verification is found to be readily soluble in acids, perfectly magnetic, and affords a

deep blue colouration upon the addition of potassium ferrocyanide, evidently aluminium-iron. After all, it is possible, but very difficult, to deposit aluminium from its aqueous solutions, and the author advises the following solution:—Dissolve aluminium hydrate in HCl, add a large excess of tartaric acid, and, lastly, an excess of ammonia, until a clear ammoniacal solution is obtained. Aluminium may be deposited by a current of 12 volts 9 amperes; employing metallic aluminium as a positive, and a sheet of brass as a negative electrode. Or replacing the positive with carbon, the deposit thus obtained in either case is perfectly white, and will bear burnishing; but, strange to say, after once covering the surface of the negative plate, a further deposit is considerably retarded, which can only be effected by further increasing the negative plate from this solution.

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ON THE VOLUMETRIC DETERMINATION OF TITANIC ACID AND IRON IN ORES.

By H. L. WELLS and W. L. MITCHELL.

THE difficulties connected with the gravimetric determination of titanic acid make a reliable volumetric method very desirable, especially for the analysis of titanic iron ores. We have therefore turned our attention to this subject, and have found that satisfactory results can be obtained by a slight modification of a process which has long been known.

About thirty years ago F. Pisani (*Comptes Rendus*, lix., 289) stated that the acid under consideration could be determined by reduction with zinc in hydrochloric acid solution, using a gentle heat, and when the violet colour no longer deepened, pouring off the liquid from the remaining zinc and titrating with potassium permanganate. Pisani gave no test analyses, and, since his process has not been generally adopted, it is evident that it has not proved satisfactory in the hands of others.

A number of years ago one of us (Wells) had occasion to analyse a large number of titanic iron ores, and attempted to use Pisani's method with the use of sulphuric acid instead of hydrochloric acid, as recommended by the originator of the process. This modification was made on account of the well-known interference of chlorides with the permanganate method, and it was found that the difficulty mentioned by Pisani, that titanic acid was liable to be precipitated by heating sulphate solutions, could be readily overcome by using a sufficiently large quantity of sulphuric acid. The results of a great many trials at that time, however, showed that the method gave very low results, and the process was then abandoned. The process used in the experiments just referred to was precisely the same as that which we now recommend, and which will be described in detail below, except that after reduction with zinc the solution was poured off, from the excess of that metal, into a beaker for titration, an operation which Pisani recommended, and which is customary in the determination of iron by this method. It is now evident that the failure of the method was due to the contact of the solutions with atmospheric air, for, while ferrous sulphate is acted upon very slowly, the sulphate corresponding to the lower oxide of titanium is very rapidly oxidised under such circumstances.

Marignac (*Zeitsch. Anal. Chem.*, vii., 112), with his accustomed skill, applied Pisani's method, soon after its publication, to the determination of titanic acid in the presence of niobic acid. He was obliged to use special conditions in order to avoid the reduction of the other acid at the same time; but the feature of his process which is interesting in the present connection is, that he reduced the titanic acid by means of a long rod of pure

zinc extending up into the neck of the flask which held the solution, and, after allowing the reduction to take place out of contact with air, he finally took out the zinc and titrated directly in the flask without transferring. Marignac gave a number of test analyses which showed that the method gave very good results, although they were a little too low with the larger quantities of titanic acid used.

We have modified the method of Pisani as improved by Marignac, by using sulphuric acid solutions, and by protecting the liquid during cooling and titration by means of carbon dioxide, and we have also arranged the process for the determination of iron along with the titanic acid. The details of the operation are as follows:—

Five grms. of very finely pulverised ore are placed in a rather large beaker covered with a watch-glass, and treated with about 100 c.c. of concentrated hydrochloric acid. A very gentle, gradually increasing heat is applied for several hours, more hydrochloric acid is added if necessary, and, when no further action is apparent, about 50 c.c. of a mixture of equal volumes of concentrated sulphuric acid and water are added, and the whole is evaporated until the sulphuric acid fumes strongly. After cooling, about 200 c.c. of water are added, the whole is heated until the sulphates are dissolved, and the liquid is filtered into a litre flask. With many titanic ores this operation will have dissolved everything except siliceous matter. If, however, some undissolved ore remains, it is ignited, to burn the filter-paper, in a platinum crucible, and the residue is fused with potassium disulphate, at a gradually increasing heat, up to low redness, until the black particles have disappeared. To the cake in the crucible several volumes of concentrated sulphuric acid are added, heat is gradually applied until the whole becomes liquid, then this is heated with a moderate volume of water to dissolve the sulphates, and the liquid is added to the main solution in the litre flask. Filtration may be omitted here, or in the case of the original solution, provided that the siliceous matter is not to be weighed.

The liquid in the litre flask is diluted to the mark and mixed, and four portions of 200 c.c. each, representing 1 gm. of ore, are taken, two of them into Erlenmeyer (conical) flasks of 500 c.c. capacity, and the other two into ordinary flasks of 350 c.c. capacity.

To determine iron, hydrogen sulphide is passed into the solutions in the ordinary flasks until they are saturated with the gas, then inverted porcelain crucible covers are placed upon the mouths of the flasks, and the solutions are heated and boiled continuously, so that air cannot enter, until the hydrogen sulphide has been completely removed. This point can be determined by testing the escaping steam with paper which has been dipped in a solution of lead acetate made strongly alkaline with potassium hydroxide. The flasks are then quickly filled to the neck with cold distilled water which has been recently boiled, —best by means of an inverted wash-bottle, directing the stream against the neck of the flask in such a way that the water does not mix to a great extent with the heavier sulphuric acid solution. If the stream of cold water does not strike the top of the neck, there is little danger of breaking the hot glass. The contents of the flasks are now rapidly cooled by means of a stream of water, transferred to large beakers, and titrated with potassium permanganate solution.

To the solutions in the Erlenmeyer flasks about 25 c.c. of concentrated sulphuric acid are added; then in each case three or four rods of chemically pure zinc, about 50 m.m. long and 6 or 7 m.m. in diameter, are attached to the loop of a porcelain crucible cover, which is larger than the mouth of the flask, by means of platinum wire wound securely around them near the middle. The length of the wire is so arranged that the pieces of zinc will be suspended in the liquid when the cover is placed on the flask. When this has been accomplished the liquid is boiled gently, so as to keep out air, for thirty or forty

minutes; then, without interrupting the boiling, a glass tube, so bent that it extends 50 m.m. or more into the flask, which is delivering a rather rapid stream of carbon dioxide, is introduced under the cover. Care should be taken to have the carbon dioxide free from air, and that hydrochloric acid which contains sulphur dioxide is not used for its generation. The flask is now rapidly cooled, and then the zinc is washed with a jet of water and removed, and the solution is titrated with permanganate in the flask while the carbon dioxide is still being passed in. The difference between the permanganate used in this case and that used for the iron alone represents the amount corresponding to the titanic acid. The factor for metallic iron divided by 0.7 gives the factor for titanic acid (TiO_2).

When a 50 c.c. burette is used, the most convenient strength for the permanganate solution is when 1 c.c. is equal to about 0.014 grm. of metallic iron, corresponding to 7.1% grms. of potassium permanganate per litre.

It is customary in this laboratory to standardise permanganate solutions by a method which very closely approaches the one described above for the actual determination of iron, so that, if any slight errors are inherent in the process, they are likely to be eliminated, because they have an equal effect upon the standardisation and the determination. The method is simple and convenient, and a large amount of experience has shown it to be very accurate. To carry out this operation, a 350 c.c. flask is half-filled with sulphuric acid (the strong acid diluted with about 8 volumes of water). This is heated to boiling with an inverted crucible cover upon the mouth of the flask, and, after the air has been expelled, about 6/10ths grm. of the purest iron wire, representing nearly the average amount of iron in 1 grm. of an ore, is dropped in, and gentle boiling is continued until it has dissolved. The flask is filled to the neck with water, cooled, and finally the liquid is transferred to a beaker and titrated.

The method of determining iron by reduction with hydrogen sulphide, although well known, does not appear to be as generally used as it deserves to be. The precipitated sulphur present in the liquid has absolutely no effect upon cold permanganate solution; but precipitated sulphides, such as copper sulphide, should be filtered off before boiling. Since concentrated sulphuric acid is an oxidising agent, care must be taken to use sufficiently dilute solution, and not boil them down until the acid becomes strong.

We have made some test analyses upon the method of determining titanic acid volumetrically. Crude potassium titanofluoride, K_2TiF_6 , was re-crystallised twice from water, and used as the source of titanium. Weighed quantities of the carefully dried salt were evaporated with sulphuric acid, and the resulting substance was treated essentially as has been described above, but with some variations in the time of boiling, the strength of the acid, and the amount of zinc used. The following table gives the results obtained in grms.:—

Potassium titanofluoride taken.	Titanium found.	Titanium calculated.	Error.
0.7638	0.1437	0.1527	-0.0090
0.6425	0.1225	0.1285	-0.0060
0.7778	0.1524	0.1555	-0.0031
0.6793	0.1308	0.1358	-0.0050
0.8226	0.1607	0.1645	-0.0038
1.0956	0.2107	0.2191	-0.0084
0.4451	0.0848	0.0890	-0.0042
0.6359	0.1215	0.1271	-0.0056
0.9004	0.1715	0.1800	-0.0085
0.4634	0.0882	0.0926	-0.0044

The results show a fair degree of uniformity, but they are invariably too low. A part of the deficiency was probably due to the impurities in the potassium titanofluoride used, for it is quite possible that certain impurities may have been increased rather than diminished by re-crystallising it, and it is exceedingly difficult to obtain any tita-

nium compound that is certainly free from all other acid-forming elements. The greater portion of the error was doubtless due to the action of air which gained access to the liquid in spite of the precautions used, and it is evident that the accuracy of determinations made by this method would be increased by adding one-twentieth or one-thirtieth to the amount of titanic acid found under the conditions that we have used.

The great influence of the action of air is shown by two determinations which were made exactly like those given in the above table, except that, after cooling in carbon dioxide, the solutions were transferred to beakers and titrated as quickly as possible.

Potassium titanofluoride taken.	Titanium found.	Titanium calculated.	Error.
0.6831	0.1078	0.1366	0.0288
0.9545	0.1535	0.1909	0.0374

The volumetric method, even without correction, will be likely to give more reliable results than those obtained by gravimetric determination, unless great care and skill are displayed in carrying out the latter. — *Journal of the American Chemical Society*, xvii., p. 878.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 114.)

The Electric Spectrum of Chloride of Calcium.—I found the chloride spectrum, when using a spark without a condenser, the same as that described by M. Bunsen; there were neither more nor fewer lines than those drawn by the illustrious Heidelberg chemist in the plate accompanying his paper on the *spark spectrum*.

For these researches I used in succession the Steinheil and Duboscq spectroscopes, the latter fitted with three or five prisms. I proved the identity when examining one by one all the lines and the position of each of them. I varied the strength of the sparks from one to five times in intensity. The result, both as regards the number and position of the calcium lines, was always the same; the only change was in the intensity of the lines and in the non-appearance or appearance of air-lines.

When using a coil with a condenser, capable of giving sparks 15 c.m. long, but which was used for giving sparks only 3 m.m. long by adjusting the platinum balls, covered with fused chloride of calcium, and either wetted or not with a saturated solution of this compound, or when sparking from the surface of an acid solution in the apparatus* previously described, I could not find the double blue line at 148 to 149 divisions on my Steinheil spectroscope in the calcium flame spectrum, whereas I saw the *first blue line*, very deeply coloured, in the same position that it occupied in the flame spectrum. I have no hesitation in saying that the double blue line does not belong to the electric spectrum of calcium. It is more than doubtful if it is one of the specific lines of the oxyhydrogen calcium spectrum, although Sainte-Claire Deville, Debray, and I have frequently seen it when working with a pure lime crucible raised to white heat in an oxyhydrogen blowpipe.

It is well known that the flame and electric spectra described by M. Bunsen are different. My observations, checked by means of a spectroscope of the same design as that used by M. Bunsen, confirm this fact. For instance, in an oxyhydrogen blowpipe, oxide, chloride, and oxychloride of calcium show green bands and lines at 52 to 53 and at 60 to 61.5 divisions on the Steinheil spectroscope, corresponding to 55 to 56 and 61.5 to 63 divisions on the Bunsen spectroscope. These bands and lines are

* See CHEMICAL NEWS, vol. lxxii., p. 248.

entirely absent from the spark spectrum of chloride in a hydrogen atmosphere; but, on the other hand, the lines at 58, 68, and 68.5 divisions on the Steinheil spectroscope, which occur in the electric spectrum, are entirely wanting in the calcium spectrum in an oxyhydrogen or oxy-coal-gas blowpipe, whatever part of the flame be examined.

Each spectrum has its own appearance, whether it be considered *separately* or by *superposition*. The oxyhydrogen calcium spectrum is unchangeable, and, notwithstanding the coincidence of certain of its bands and one line, it cannot be made to coincide with the *electric* calcium spectrum.

The above observations and the conclusions I arrived at date from seven to eight years ago, as I said in the first chapter; since those researches were carried out, I have again converted oxide of calcium into chloride, both by pure dry hydrochloric acid gas, sheltered from air, and by the action of heat on a mixture of pure oxide of calcium and chloride of ammonium, in the air. Whilst carrying on all the operations in closed platinum vessels, I failed every time to procure platinum balls covered with chloride of calcium fused in the air, which would not show the sodium line when analysing a spark flashed in air or hydrogen.

I beg to refer any reader who wishes for details of these facts to the preceding chapter.

I used samples of exceptionally pure chloride to obtain a spectrum, both in an oxyhydrogen blowpipe and in an induction spark, working in air or in a hydrogen atmosphere.

When using Steinheil and Duboscq spectroscopes, I found in an oxyhydrogen blowpipe, after the dissociation of the chloride and the formation of oxychloride, the flame spectrum of oxide of calcium did not show even a momentary trace of the sodium line.

When making, by means of a Duboscq spectroscope with three or five prisms, or a large Hilger spectroscope with three prisms of Iceland spar, an analysis of an electric spark or discharge saturated with chloride in an atmosphere of pure hydrogen, I once more found the extreme accuracy of M. Bunsen's description.

The flame and electric spectra of chloride of calcium differ both in the *number* and *position* of their component lines.

The oxyhydrogen calcium spectrum alone shows a *single really sharp line*,—the blue line at 125.5 on the Steinheil, or 155 on the Bunsen, spectroscope. The other lines consist of more or less diffuse bands, and are not capable of being resolved by the instruments at my disposal. Every line in the electric spectrum is sharp, excepting *two or three at most*. The exceptions consist of groups of very close lines, which my instruments are not capable of separating.

With the object of satisfying myself as to the permanence of the number and position of the lines in the electric spectrum of calcium, I examined the arc spectrum of calcium under various conditions.

For this purpose I made an electric arc charged with calcium by means of a battery of *thirty* of the largest Bunsen cells, using pure carbon electrodes. The negative electrode, 10 c.m. long by about 5 m.m. diam., ended in a point which was coated with freshly-made fused oxychloride of calcium; the positive electrode, 10 c.m. long by about 1 c.m. diam., ended in a flat surface with a cavity. The flat rim was coated, and the cavity was filled with freshly-made oxychloride of calcium. The electrodes, arranged *vertically*, were inserted into strong *insulated* brass rings, working, by means of racks, on a varnished glass rod.

Having put the electrodes in contact, I formed the arc by heating the point of contact, and melting the oxychloride of calcium by means of a hydrogen and air blowpipe. I made observations, on the one hand, of the electrodes covered with oxychloride in contact, and, on the other hand, of the electrodes covered with oxychloride separated by the interval forming the arc.

As analysers, M. Rommelaere and I used in succession:—

1. The Steinheil spectroscope;
2. The Duboscq spectroscope, fitted either with three or five prisms;
3. The large Hilger spectroscope, fitted with three or six Iceland spar prisms.

Whatever spectroscope we used, the results were the same, as regards the calcium spectrum, when the electrodes were in *contact* and when they were separated,—that is to say, when we observed the arc properly so called.

Spectrum analysis of the incandescent part of the electrodes in *contact* showed a very bright continuous spectrum, with broad lines, so diffuse that it was impossible to decide whether they were due to a flame spectrum or to an electric spectrum, or to a mixture of the two spectra. The simple blue line was extremely sharp; the two broad, indistinct, deep red and yellowish red lines were the same as in the discharge spectrum.

On separating the electrodes, so as to form an *arc*, and looking exclusively at the middle of the arc, I saw a continuous spectrum, showing both the electric spectrum of calcium and the carbon spectrum in the form of *fine* lines, produced by the resolution of the carbon bands; the *two red calcium lines* were broad and hazy, but less so than in the spectrum made with the electrodes in contact. The luminosity in the arc was evidently greater.

I did not see in the arc spectrum the two blue lines seen in the spectrum of the *inner cone* of an oxyhydrogen and oxy-coal-gas blowpipe charged with calcium.

By putting chloride of calcium into the cavity in the positive electrode as it was volatilised, by means of a small spatula of pure carbon, I was enabled to reproduce the two spectra mentioned above *at will*, and for as long a time as was required for the observations, changing one spectroscope for another.

At the instant of introducing chloride of calcium into the arc, both M. Rommelaere and I always saw the sodium D line in the spectrum; but after a few moments it was scarcely more visible than in an arc without calcium passing in the air of the large room we were working in.

I found that an electric arc *charged with calcium* was quite *blue*; the envelope of the arc was bluish white, but above the arc I observed that deep brown colour characteristic of flames charged with pure calcium compounds at a high temperature.

Throughout these observations I saw no air lines, even when separating the electrodes so far as to break the arc.

When revising the spectroscopic researches described above, in collaboration with M. Depaire, we found that every observation was perfectly accurate, both for the flame spectrum and the electric spectrum of calcium.

It is undeniable that the flame and electric spectra of chloride of calcium are different, and that, by the means known to us, it is impossible to change the one into the other.

To satisfy ourselves as to the permanence of the electric spectrum of calcium, M. Depaire and I employed the powerful currents used for examining the electric spectrum of lithium.

For this purpose we formed an electric arc successively:—

1. By means of a battery of thirty-three Julien accumulator cells, giving at the terminals 10 amperes and 70 volts;
2. By means of a Gramme and Siemens dynamo coupled. Instead of a Foucault regulator we used a Gerard regulator, which gave a steadier arc than the former.

The pure carbon electrodes, coated with oxychloride of calcium, were arranged in the same way as described for the researches on the electric arc charged with lithium.

One of us used at first a Duboscq spectroscope, similar to that used by M. Lecoq de Boisbaudran; and after-

wards a Hilger spectroscope with two half-prisms and lenses of quartz; whilst the other used a new direct vision spectroscope with flint-glass prisms, designed by Messrs. Living and Dewar.

Having put the electrodes in contact, and completed the circuit by melting the oxychloride with a hydrogen and air blowpipe, we found, both with the current from the accumulators, forming an arc about nine m.m. long by eight m.m. diam., and with the current from the coupled dynamos, forming an arc about two and a half c.m. long by eight m.m. diam., the spectra were the same as those seen with the current produced by thirty Bunsen cells; that is to say, that spectrum analysis of the bright light, formed whilst the electrodes coated with chloride were in contact, showed a continuous spectrum, on which was superposed a calcium spectrum so diffused that it was impossible to define it, and that analysis of the arc proper showed a continuous spectrum, on which was superposed simultaneously the calcium spectrum of an electric discharge and a carbon spectrum as seen in an arc passing between pure carbon electrodes. In both cases the red lines are diffused, but very much less in the arc spectrum than in the induction spectrum; the diffused lines will probably be eventually resolved into fine lines.

The sodium D line *always* appeared in the chloride spectrum as soon as the arc was formed; but, after a few moments, this line became fainter, and at last appeared only as clearly as it was seen in an arc in the same atmosphere, and with the same recently heated electrodes.

In the calcium arc formed by the two coupled dynamos, the length of which was about 2½ c.m., the arc proper was coloured blue, the lower part of its envelope white, and the upper part of its envelope chocolate-brown.

However quickly the chloride of calcium occluded sodium from the medium in which it was made and kept, there was no connection between the luminous spectra of sodium, potassium, and lithium, and flame spectrum of oxide or chloride of calcium, and the electric spectrum of this last chloride.

It is impossible, by raising the temperature, to change the flame spectrum to the electric spectrum, and *vice versa*. Under the conditions in which I carried on my researches, these two spectra are unchangeable; they are specific, in the same degree and under the same conditions, as the spectra of sodium, potassium, and lithium.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 20th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. Jervis E. Foakes and C. E. Harrison were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Henry Thomas Durant, c/o Messrs. Loewenstein and Co., Johannesburg, South Africa; Herbert Edwin Macadam, Adam's Chemical Co., Victoria Docks, E.; Charles H. Reissman, B.A., B.Sc., Saxony Villa, Oppidans Road, Primrose Hill, N.W.; James Edward Shum Tuckett, M.A., 14, Hyde Road, Eastbourne.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As *Vice-Presidents*—Professor James Dewar, F.R.S., and Professor W. A. Tilden, F.R.S., *vice* Dr. E. Atkinson and C. O'Sullivan, F.R.S.

As *Ordinary Members of Council*—Dr. Forster Morley, Dr. G. H. Morris, Mr. J. W. Rodger, and Professor Arthur Smithells, *vice* Professor H. Dixon, F.R.S., Mr. R. J. Friswell, Dr. Kipping, and Dr. W. P. Wynne.

Messrs. Bertram Blount, H. Brereton Baker, and Dr. J. Shields were appointed to audit the Society's accounts.

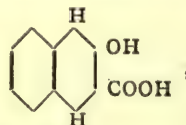
The following were duly elected Fellows of the Society:—

John Allan, William Henry Barker, B.Sc., William Henry Bentley, B.Sc., Maurice Blood, B.A., Joseph Edwin Algar Blyde, Joseph John Bowley, Herbert Lister Bowman, B.A., Daniel Bray, James Kerry Burbridge, Hugh Charles Herbert Candy, B.Sc., James Craig, M.A., B.Sc., Frank Dixon, Arnold Eiloart, Ph.D., Thomas Ewan, B.Sc., Ph.D., Charles James Pemmeller Fuller, Walter Thomas Grise, William Harrington, James William Helps, Albert Howard, Ernest Haynes Jeffers, James Johnstone, Cass L. Kennicott, Laurence W. Mathieson, Joseph Edward Morrison, Harold Rostron, B.Sc., Thomas Francis Rutter, B.Sc., Charles Edward Sage, Arthur Philip Salt, Peter B. Scotland, Aitken Migget Simpson, Amrita Lal Sircar, L.M.S., Henry George Smith, Benjamin Bernard Turner, B.Sc.

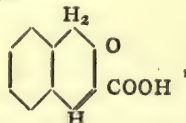
Of the following papers those marked * were read:—

*21. "The Origin of Colour. No. XI. The Yellow Colour of 2:3-Hydroxynaphthoic Acid." By HENRY E. ARMSTRONG.

Möhlau, in a recent most interesting note (*Ber.*, 1895, 3100), draws attention to the remarkable fact that 2:3-hydroxynaphthoic acid and a number of its derivatives are coloured (yellow) substances. On account of this peculiarity, he proposes to substitute for the conventional formula.



the isodynamic expression—



and seeks to explain the fact that the ethylic salt of the acid dissolves in alkali, yielding a yellow solution, by the assumption that a yellow sodium derivative is produced by the displacement of one of the two hydrogen atoms in position 1.

These new formulæ do not seem to harmonise with any conception which can at present be formed as to the inter-relationship of colour and structure, a subject to which the present writer has so often directed attention in communications to the Society (compare *Proc. Chem. Soc.*, 1890—93). It is not difficult, however, to account for the appearance of colour in such a case by an assumption similar to that already made use of by him in the case of certain terephthalic and other benzenoid compounds, as well as of certain quinoline derivatives (*Proc. Chem. Soc.*, 1892, 103; 1893, 13, 52, 55, 206; *Trans.*, 1892, 789).

Whatever the exact structure of naphthalene may be, it is presumably centric in form, and not ethenoid, although its great activity in comparison with that of benzene may be regarded as evidence of a strong tendency to change its form. If it be supposed that, owing to the strong tendency which oxygen exhibits in so many benzenoid compounds to assume the keto-form, 2:3-hydroxynaphthoic acid can pass from the hydroxy- to the isodynamic keto-form, and in so doing affect the structure of the cycloid itself, in the manner shown by the following symbols:—



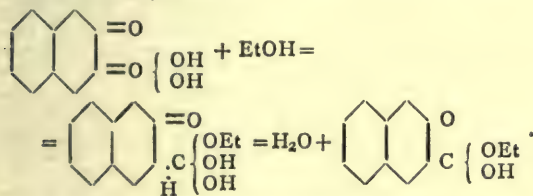
the yellow colour is accounted for without difficulty, as such a compound would be not only an orthoquinonoid derivative of naphthalene, but also an orthoquinonoid derivative of benzene. The "etheral salt" of such an acid would contain a free hydroxyl group, and might therefore well be acid.

The behaviour of the acid with phenylhydrazine, to which Schöpf has just drawn attention (*Ber.*, 1896, 265), is without difficulty expressed by the formula here suggested.

*22. "Note on Etherification." By HENRY E. ARMSTRONG.

Möhlau, in the paper referred to in the foregoing note, calls attention to V. Meyer's observation that the 2:3-acid in question is converted into an ethylic salt more readily than is the isomeric α -hydroxynaphthoic acid, and regards this as strong evidence in favour of his view of the constitution of the acid.

An acid represented by a formula such as is suggested above would probably be particularly prone to combine with an alcohol, thus—



Attention is now drawn to this with the object of raising the question whether some such explanation may not apply to the remarkable generalisation at which V. Meyer has arrived in the case of diortho-substituted acids, and which he has sought to justify by introducing space considerations.

The formation of a salt is presumably preceded by that of a combination of acid and "alkaloid," from which water is then eliminated. Just as the acid-attracting power of the NH_2 radicle in aniline is affected by the introduction, say, of chlorine, so, in like manner, the "alkaloid" attracting power of the carboxyl group may be assumed to vary as radicles are introduced in its neighbourhood in place of hydrogen—more particularly in the case of benzenoid compounds.

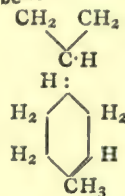
Apparently such effects are not sufficiently taken into account—the observations on the dimethylanilinesulphonic acids made in the writer's laboratory by Miss Evans (compare *Proc. Chem. Soc.*, 1895, 235), may be referred to as of considerable interest from this point of view, showing as they do that the mere introduction of two methyl groups into the NH_2 -group in place of the hydrogen altogether modifies the character of the compound, rendering it insensitive to the action of bromine in a most remarkable manner. It is intended to make experiments to ascertain if the introduction of different alkyls into the carboxyl group affect the behaviour of acids in any similar manner.

*23. "The Relation of Pinene to Citrene." By HENRY E. ARMSTRONG.

A. v. Baeyer in his recent (13th) note on orientation in the terpene series, shows in a most interesting manner that the genetic connection existing between pinene and citrene is far closer than has hitherto been supposed. It may, therefore, be desirable to briefly put on record an idea with reference to pinene which has long been in the writer's mind, and which has led him to regard the problem of its constitution from a point of view somewhat similar to that by which v. Baeyer appears to have been guided.

The fact that, under certain conditions, pinene behaves as a monethenoid compound, and yet under others readily gives derivatives, such as the citrene dihydrochlorides, led him, several years ago, to consider the possibility of

its being a trimethylene derivative, the simplest expression for which would be—



It is unnecessary to point out how such a compound would pass into a citrene-dihydrochloride such as may be derived from Tiemann's citrene formula, the formation of which from a dipentamethylene derivative such as pinene is represented to be by both Bredt and Tiemann is very difficult to understand—not to say eminently improbable.

The explanation of the formation of a compound having the properties of the hydrochloride obtained from pinene—artificial camphor—offers perhaps the greatest difficulty at present. This compound can scarcely be a direct derivative of pinene, and seems to be closely related to camphor—in fact, the writer has obtained a small quantity of camphoric acid by its oxidation with nitric acid. It appears not improbable that some more or less profound change attends its formation, and, with the aid of the formula given above, it would not be difficult to represent the production from the trimethylene radicle of a new penta- or methyl-tetramethylene ring attached to contiguous carbon atoms of the hexamethylene ring, and thus to arrive at a formula such as the writer long ago attributed to camphor.

That many of the derivatives obtained from camphor are the end-products of a series of analytic and synthetic changes there can be no doubt. It is impossible to explain the formation of substances so different as cymene, metacymene, ethyldimethylbenzene, carvacrol, and acetylorthoxylene in any other way. At one time we thought but of its relation to cymene; latterly the relation of camphor to trimethylsuccinic acid has monopolised attention: but it may well be that the latter, like the former, is an elusive support, and owes its formation to atomic redistribution.

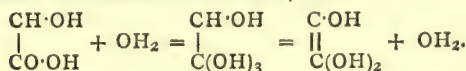
It may be pointed out that "artificial camphor," pinene nitrosochloride, and pinene dibromide differ in a remarkable and significant manner in optical properties, the first alone being optically active. It is to be remembered that the carbon atoms which are connected by an ethenoid linkage in pinene cannot be the origin of its optical activity, and, whatever its formula, it must be one containing at least one asymmetric carbon atom. But, this being the case, it is difficult to understand how the addition, either of bromine or of nitrosyl chloride, can give rise to optically inactive products capable of affording an inactive pinene; the occurrence of "racematisation" in such a case would seem to indicate that the region in which the asymmetric carbon is situated also becomes affected, although, apparently, but temporarily; i.e., whatever be the change, it is subsequently reversed, even when pinene is converted into the nitrosochloride. If we cannot accept this conclusion, we must admit that the formulæ hitherto attributed to pinene are all unsatisfactory expressions to a far greater extent than we have ever supposed. The difficulty, it may be added, is greater in the case of such a formula as Tiemann's—as this contains two asymmetric carbons—than in the case of those proposed by v. Baeyer, or by the writer.

A similar argument is applicable in the case of camphor. If the argument of the following note be admitted, the production of an inactive campholide on reduction of camphoric anhydride (Haller, *Comptes Rendus*, 1896, 295) may, in fact, be regarded not only as a proof that the CO group undergoing reduction is connected with an hydro-genised asymmetric carbon atom, but also as evidence of the presence of but a single asymmetric carbon in camphor.

*24. "The Conditions involved in the Occurrence of Inversion in the case of Asymmetric (Optically Active) Compounds." By HENRY E. ARMSTRONG.

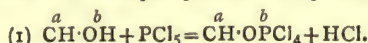
Having formed the opinion that the changes which attend the production of what are supposed to be pinene derivatives merit much closer attention, the writer has been led to carefully consider Walden's recent very remarkable observations on the formation from each of the two active malic acids by means of phosphorus pentachloride or bromide of an oppositely active chloro- or bromo-succinic acid, from each of which in turn a malic acid of its own order of activity may be obtained (*Ber.*, 1896, 133). It does not appear difficult to explain these results without any modification of our current theory, and attention is now called to considerations which, perhaps, may prove to be of importance in discussions of the behaviour, and of other questions relating to, asymmetric compounds.

When optical inversion is effected by hydrolytic agents, in the case of an aldose, or of a ketose or acid, it is probable that, in the first instance, the keto-group becomes hydrated, and that either an "aldehydrol," $\text{CH}(\text{OH})_2$, or a "ketohydrol," $\text{C}(\text{OH})_2$, or an "acidhydrol," $\text{C}(\text{OH})_3$, is produced. When water is withdrawn from such compounds, if the water be formed from an OH-group of the hydrol complex and a hydrogen atom attached to the carbon contiguous to that of the hydrol complex, an ethenoid derivative will be formed, thus—

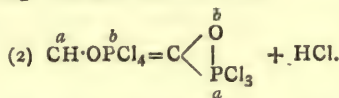


On hydration, according as hydration takes place at the one or the other junction of the ethenoid linkage, such a compound will afford one or the other of the two possible asymmetric forms, and if, as in the case of tartaric acid, the compound be symmetrical, it is to be expected that the two forms will be produced in equal proportions. But if an unsymmetrical compound be thus changed, such as a hexose or an acid like gluconic acid, it is to be expected that the severance will take place to a greater extent at one of the two junctions, and in some cases perhaps only at one. The striking results recently obtained by Lobry de Bruyn, and all E. Fischer's observations, are in accordance with this view, which, in fact, is the generally accepted one.

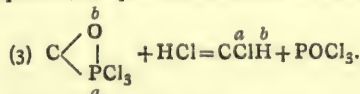
When malic acid is acted on by, say, phosphorus pentachloride, probably the first action to occur is one involving the formation of a chlorophosphonium compound, thus,—



The next stage in the change may be assumed to be one involving "internal condensation,"—



Supposing that this compound be then acted on by hydrogen chloride and resolved into chlorosuccinic acid and phosphorus oxychloride, if the attack became directed by the phosphorus, so that the chlorine took up the position of the phosphorus, complete inversion would be effected :—



It will be obvious that such an explanation may be of general application, especially in connection with the exclusive production, under natural conditions, of a single asymmetric form.

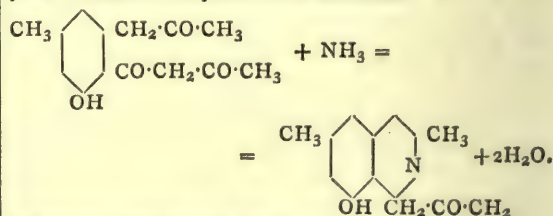
*25. "The Production of Naphthalene and of Isoquinoline Derivatives from Dehydroacetic Acid." By J. NORMAN COLLIE, Ph.D., and N. T. M. WILSMORE, M.Sc.

It was shown by one of the authors (*Trans.*, lxi., 329), that, under certain conditions, diacetylacetone condenses forming a yellow crystalline compound, apparently a benzene derivative, and that this further condenses easily, forming a second yellow compound, which was shown to be a derivative of naphthalene.

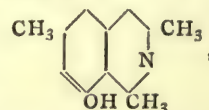
On the average, dehydroacetic acid yields about a quarter of its weight of the first compound. A dioxime of the first yellow compound has been prepared in a nearly pure state. By distilling the diacetate of the second yellow compound with zinc dust, a naphthalene hydrocarbon, m. p. 75–78°, has been prepared. Its composition agrees well with that of a dimethylnaphthalene. On oxidation with dilute nitric acid it yields an acid, giving the fluorescein reaction. Analysis of the silver salt of this acid agrees with the composition $\text{C}_9\text{H}_6\text{O}_2\text{Ag}_2$; and the melting-point, 115–120°, coincides fairly well with that found for benzene 1 methyl 3, 4 dicarboxylic acid (*Ber.*, 1892, 2108). By the action of strong sulphuric acid on the second yellow compound (dimethylacetodinaphthol), a colourless substance results.

By the action of strong ammonia on the first yellow compound, a yellow basic substance ($\text{C}_{14}\text{H}_{15}\text{NO}_2$) is produced, soluble in water and in alcohol, forming intensely yellow solutions. The chloride and platinichloride were prepared and analysed. On heating with strong sulphuric acid, acetic acid is given off, and the sulphate of another base is left. This base has the composition $\text{C}_{12}\text{H}_{13}\text{NO}$. On oxidation it yielded an acid, which appeared to be a lutidine dicarboxylic acid, $\text{C}_9\text{H}_9\text{NO}_4$.

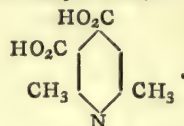
The authors consider it probable that these bases are derivatives of isoquinoline formed by condensation of the yellow benzene compound with ammonia.



The second base would be—



and the lutidine dicarboxylic acid,—



*26. "Note on a Difficulty encountered in the Determination of Nitrogen by the Absolute Method." By WYNDHAM R. DUNSTAN, F.R.S., and F. H. CARR.

The percentage of nitrogen in aconitine determined by the soda-lime process, using the base, or by the absolute method, using the hydrochloride, agrees well with that calculated from the formula $\text{C}_{33}\text{H}_{45}\text{NO}_{12}$, which is 2.1 per cent. A few years ago, Richards and Rogers (*Chemist and Druggist*, xxxviii., 242) stated that when the amount of "nitrogen" in aconitine is determined in the usual manner by the absolute method, it is found to correspond with nearly twice the percentage calculated from the formula given above, and they, therefore, proposed to alter the formula of aconitine to $\text{C}_{33}\text{H}_{43}\text{N}_2\text{O}_{12}$, in accordance with the results of their determinations. At that time the present writers were unable to look into the cause of these high results, but they were satisfied as to the accuracy of previous determinations (with the hydrochloride), showing

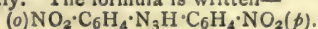
that the molecule of the alkaloid contains but one atom of nitrogen. Recently they have had occasion to determine the nitrogen in the base by the absolute method, the air being expelled from the combustion-tube by carbon dioxide, and the gas collected in an azotometer. They were surprised to find that over 4 per cent of gas was obtained instead of 2.1 per cent, the calculated quantity. The determination has since been repeated by four independent observers, every precaution being taken to ensure complete combustion by employing a long layer (about 60 c.m.) of red-hot copper oxide, and by conducting the burning slowly. The percentages obtained were 4.4, 5.3, 5.1, 3.8, 4.0, 4.1, 4.3. The highest percentages were obtained when the burning was conducted at about the usual rate, the lowest numbers by burning extremely slowly and maintaining the temperature as high as possible throughout the process. Similar results were obtained when the combustion was conducted in a vacuum, and the gas drawn off through a Sprengel pump in the manner suggested by Frankland and Armstrong. The hydrochloride of the alkaloid, however, when burned in either way gives a percentage only slightly higher than the calculated amount. Strychnine and some other typical nitrogenous organic compounds have been burnt in precisely the same manner as aconitine, but the percentages found were, as usual, only slightly higher than those calculated from the formula.

A quantity of this gas having been collected in different experiments which had given too high results, a complete analysis of it was made. Nitric oxide and carbon monoxide were absent. By exploding with excess of oxygen, measuring the contraction, and absorbing the carbon dioxide, methane was proved to be present. Estimating the methane in the mixed gas, and deducting it from the total volume taken, the nitrogen amounted to almost exactly 2.1 per cent, corresponding with that calculated from the formula $C_{33}H_{45}NO_{12}$.

Experiments made with artificially prepared mixtures have shown that when largely diluted with nitrogen, methane is burnt very slowly and with difficulty by red-hot copper oxide. In conducting the process in the usual manner the influence of the carbon dioxide used to expel the air from the tube no doubt greatly aggravates the difficulty. Aconitine seems to be exceptional in giving rise to so much methane during combustion. Possibly the difficulty might be overcome by mixing the alkaloid, not merely with finely powdered copper oxide, but also with a more powerful oxidising agent, as, for example, lead chromate. Neither aconitine hydrochloride, benz-aconine, nor aconine hydrochloride present this anomaly, and it has been observed that if aconitine is introduced into the tube along with a little cuprous chloride, the percentage of gas obtained corresponds very nearly with the calculated quantity.

27. "Mixed Diazoamides containing an Orthonitro-Group." By RAPHAEL MELDOLA, F.R.S., and FREDERICK WILLIAM STREATFEILD, F.I.C.

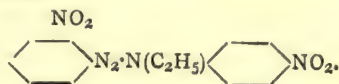
Orthodinitrodiazoamidobenzene, which was prepared and described by the authors in their last communication on this subject (*Trans.*, 1894, 52), does not appear to be capable of ethylation by the usual methods (*loc. cit.*). As this is the first exception that has yet been found to the general method of alkylating the diazoamides introduced by the authors in 1886 (*Trans.*, 1886, 624), it became of special interest to ascertain whether the usual triplet of isomerides could be prepared when an orthonitro-group was present on one side of the chain of nitrogen atoms. The mixed diazoamide from ortho- and para-nitraniline was prepared by both methods of combination in the usual way, and the product found to be identical irrespective of the order of diazotising. So far the production of the compound is quite normal. After crystallisation from alcohol it consists of golden yellow scales melting with decomposition at $192-193^\circ$ when the temperature is raised rapidly. The formula is written—



The compound is decomposed by excess of strong hydrochloric acid at ordinary temperatures into the usual mixture of four products, viz., ortho- and para-nitraniline and the corresponding diazo-chlorides. It has the acid characters common to all the dinitrodiazoamides, dissolving in alkaline solutions with a reddish colour, and being precipitated unchanged by acids. By the action of ethyl iodide on the potassium salt in alcoholic solution the ethyl derivative is obtained in the usual way. The latter consists of orange needles melting at $177-179^\circ$.

A special attempt was made in this case to separate the mixed diazoamide into isomerides by fractional ethylation, but the result was negative, the product being simply a mixture of unethylated compound (m. p. $192-193^\circ$) and the ethyl derivative (m. p. $177-178^\circ$). Under all circumstances, the ethylation of this diazoamide is incomplete, a certain amount of unchanged substance being left in the mother liquor, even when potassium hydroxide and ethyl iodide are used in excess.

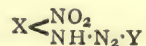
The behaviour of the ethyl derivative towards hydrochloric acid is quite exceptional, and the products of its decomposition are ethyl-*p*-nitraniline and orthonitrodiazo-benzene chloride. This is the first instance which has come under our observation in which an alkyl-diazoamide from the direct alkylation of a mixed diazoamide has given only two instead of four products on decomposition by acid. This ethyl derivative is also remarkable for its stability towards hydrochloric acid, as it had to be kept at a temperature of about $80-90^\circ$ for some hours in presence of a large excess of acid before decomposition was complete. Not a trace of nitrogen was evolved during the decomposition. The products were identified by filtering the cold acid solution into an alkaline solution of β -naphthol (*Trans.*, 1887, 438) and collecting the bright red precipitate which at once formed. The latter, after washing with water, was extracted with hydrochloric acid, which removed ethyl-*p*-nitraniline; melting-point of nitrosamine $119-120^\circ$ (*Trans.*, 1886, 631). The red residue proved to be orthonitrobenzeneazo- β -naphthol, m. p. 210° (Meldola and Hughes, *Trans.*, 1891, 374). These results indicate for the ethyl derivative the definite formula—



This view was confirmed by combining diazotised orthonitraniline with ethyl-*p*-nitraniline when the same compound (m. p. $177-179^\circ$) was obtained, and not an isomeride.

The explanation of the exceptional behaviour of this ethyl derivative is bound up with the general question of the "protecting influence" of a nitro-group in the ortho-position, as shown more especially by the recent researches in Victor Meyer's laboratory, which bring out very clearly the influence of ortho-substituents in preventing alkylation of the carboxyl group.

The System—



is incapable of being alkylated when NO_2 and NH are in the ortho-position. An attempt to prepare the isomeride by the action of diazotised paranitraniline on ethyl-*o*-nitraniline brought out still more forcibly the influence of the orthonitro-group. Combination could not be effected under any of the conditions which so readily furnish the other alkyl-diazoamides; paranitrodiazo-benzene chloride does not appear to have any action on ethyl-*o*-nitraniline.

It may be of interest to state in conclusion that these results are of great importance as establishing the fixity of the alkyl group when once introduced into a diazoamide. If this group were at all "labile," it might have been expected that by the action of diazotised paranitraniline on ethyl-*o*-nitraniline the same compound would have been obtained as by the action of diazotised

orthonitraniline on ethyl-*p*-nitraniline. In the former case, as we have proved, the compounds remain for days in contact without combining. The difficulty which we have experienced in preparing ethyl-*o*-nitraniline is also due to this same influence of the orthonitro-group. Since orthodinitrodiazoamidobenzene cannot be ethylated, we were unable to prepare it by the decomposition of this compound. Attempts to ethylate orthonitraniline directly gave unsatisfactory results, as also did the published methods (*Beilstein*, vol. ii., 332). The simplest method, according to our experience, is to heat orthonitrophenol ether (ethyl) with alcoholic ethylamine in a sealed tube for twelve hours at 150°.

28. "Allyl *p*-Dinitrodiazoamidobenzene: a Study of the Relations between Melting-point and Constitution." By RAPHAEL MELDOLA, F.R.S., and FREDERICK WILLIAM STREETFEILD, F.I.C.

As the introduction of alkyls into diazoamides always lowers the melting-point, the lowering being greater the greater the weight of the homologous radicles introduced, the above compound was prepared with a view to ascertaining whether the same rule holds good for unsaturated radicles. It was found that paradintradiazoamidobenzene could be quite readily converted into an alkyl derivative by the action of potassium hydroxide and allyl iodide in the usual way. The pure compound forms small yellow needles, m. p. 164—165°.

0.0826 gave 15.1 c.c. moist nitrogen at 14.5° and 759.4 m.m. = 21.42 N. $(p)NO_2 \cdot C_6H_4 \cdot N_2 \cdot N(C_3H_5) \cdot C_6H_4 \cdot NO_2(p)$ requires N = 21.40 per cent.

The melting-point of the original compound is about 236° (if the temperature is raised very rapidly), of the methyl derivative 219°, of the ethyl derivative 191—192°, and of the benzyl derivative 190° (*Trans.*, 1887, 112). Taking the upper limit of temperature at which the original compound decomposes (236°) the depression produced by methyl is 17°, ethyl 44°, benzyl 46°, and allyl 71°. It thus appears that the unsaturated radicle lowers the melting-point to the same extent (27°) as the difference between the methyl and ethyl derivatives, and so far allyl may be said to exert a normal influence. In other words, the difference between the allyl and ethyl derivative is the same as between the ethyl and methyl derivative. Since benzyl produces practically the same lowering as ethyl, it would further appear that the nature of the group in direct combination with the nitrogen atom is of paramount influence, and that any other radicles associated with this group, such as C_6H_5 in $CH_2 \cdot C_6H_5$, are of subsidiary influence. The actual weight of the introduced radicle is thus of small importance as compared with its constitution.

NOTICES OF BOOKS.

Petroleum: a Treatise on the Geographical Distribution and Geological Occurrence of Petroleum and Natural Gas; the Physical and Chemical Properties, Production, and Refining of Petroleum and Ozokerite; the Characters and Uses, Testing, Transport, and Storage of Petroleum Products, and the Legislative Enactments relating thereto; together with a Description of the Shale Oil and Allied Industries. By BOVERTON REDWOOD, F.R.S., F.I.C., Assoc. Inst. C.E., V.-P. Soc. Chem. Industry, F.C.S., F.G.S., F.R.G.S., &c. Assisted by G. T. HOLLOWAY, Assoc. R.C.S., F.I.C.; and other Contributors. In Two Volumes, with numerous Maps, Plates, and Illustrations in the Text. Vol. I. London: Charles Griffin and Co. (Ltd.). 1896. 8vo., Pp. 900.

The gigantic importance, in modern industry and commerce, of petroleum and its products, fully justifies the appearance of a work of the encyclopædic character of

the two volumes before us, and their authorship could not have devolved upon a more qualified expert than Mr. Boverton Redwood. The subject is here viewed under its multifarious aspects, chemical, geological, engineering, and sanitary. The author has had the opportunity of visiting and reporting on the petroleum fields and refineries of the United States and of Russia, and has, in addition, collated the researches of others.

An inspection of the accompanying map of the world will convince us of the very extensive distribution of this useful mineral. Petroleum wells seem most plentifully distributed in the Eastern hemisphere, in a belt extending from the Malay Islands, through India, Persia, the shores of the Caspian, Southern and Central Europe as far as Spain. In Siberia and Northern Europe petroleum has been as yet rarely and sparingly discovered. With the exception of Morocco and Egypt, and one locality near Cape Coast Castle, Africa is devoid of this inestimable product. Australia is equally poor.

In the Western Hemisphere we encounter petroleum in a belt stretching from Alaska in a south-easterly direction to the Alleghanies, where it is most splendidly developed. It is then met with more sporadically in Mexico, the West Indies, Colombia, Peru, down to near the mouth of La Plata.

We have no right to say that petroleum may not exist to an important extent in the countries where it has not yet been obtained, but so far as research has gone it seems to affect the volcanic regions of the world. Hence its scanty occurrence in Africa, Australia, and Brazil,—its remarkable association with salt and with mud volcanoes, as in Arrakan.

The origin of petroleum has given rise to much speculation and research, though it cannot be said that any one theory has obtained general acceptance. The view of an inorganic origin, supported by such eminent authorities as Mendeleeff, and Berthelot, Bischoff, and others, is still doubtful. The theory of its origin from organic remains, animal or vegetable, is upheld by Sterry Hunt, Newberry, Packham, Höfer, Orton, and others, and appears to be in the ascendant. Our author, however, judiciously concludes that no one theory seems to account for all the phenomena of the production of petroleum in every case.

A large portion of the second volume is devoted to the legislation adopted in different countries touching the importation and storage of petroleum. It is to be noted that the original British standard, 100° F., as fixed in 1862, has been withdrawn, and our present standard, established in 1879, is 73° F. This standard is generally considered as perilously low, but any administration which should propose an amended standard would incur the bitter hostility of all persons interested in the trade. In the State of Illinois the limit fixed is 150°, and we learn that inferior oils are with all diligence shipped off to Britain.

Mr. Boverton Redwood has made in these volumes a splendid contribution to our technical literature.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxii., No. 3.

Mercury in Asturias.—A. Dory.—Asturias produced, in 1883, 4000 bottles of mercury of 34.503 kilos. each.

Deposit of Cinnabar at Gratwein-Eisbach, in Styria.—Jules François.—The cinnabar of Gratwein yields 5.72 per cent of mercury for the richer kind of ore, and 4.12 per cent for the poorer kind.

Researches placed at the Service of Medicine and Surgery by Electrical Science.—Prof. Eric Gérard.—The effects of this potent agent may assume a mechanical form, as in the case of neuro-muscular contractions, and the transfer of liquids and dissolved salt with the current. The effects taking a chemical form in electrolysis are utilised for decomposing tissues or causing reagents to pass through them. Lastly, we have observed thermic results. But electricity demands to be managed with discernment. I wish that the faculties of medicine would require one of their members to teach the principles of electro-therapy.

The British Imperial Exhibition at Montreal.—This Exhibition will open on May 24th next, and will have sixteen sections, — i. e., architecture and forests, means of transport, general industries, food industries, sea and river fisheries, hygiene, machinery, lighting, industrial arts, heating, geology, furniture, protection to life, horticulture, insurances, various.

MISCELLANEOUS.

The Madrid Aërolite.—In connection with the explosion of an aërolite, which occurred in the atmosphere at Madrid, on the 10th of February last, at 9.30 in the morning, during bright sunshine, and throwing the whole city into a state of consternation, the Queen Regent of Spain has caused the following letter to be addressed to Dr. Phipson, of Putney, author of a work on these curious phenomena:—"Madrid, 20 February, 1896. Sir,—Having had the honour of placing in the hands of Her Majesty the Queen Regent the copy you have kindly sent her of your work, 'Meteors, Aërolites, and Falling Stars,' my august Sovereign has deigned to command me to thank you in her Royal name for sending her so interesting a work. Accept, Sir, the expression of my distinguished consideration.—(Signed) Count MORPHY."

The Wiesbaden Chemical Laboratory.—The Chemical Laboratory of Professor Dr. R. Fresenius has been attended by fifty-five Students during the Winter Session of 1895–96. Thirty-nine of these were German, six were English, and two Belgian, and the remaining eight came respectively from the United States, Norway, Sweden, Holland, Russia, Italy, Spain, and Australia. There were three assistant demonstrators in the several teaching departments, and twenty-three assistants in the Versuchsstationen (private laboratories). The Royal Prussian Minister of Education has given the certificate of qualification as food analyst to Prof. Dr. R. Fresenius, Prof. Dr. H. Fresenius, Dr. W. Fresenius, and Dr. E. Hintz. In addition to these Professors of the Establishment there are the following:—Dr. G. Frank (Bacteriology and Hygiene), Dr. W. Leng (Microscopy), Dr. L. Grünhut (Technology), and Mr. T. Brahm (Technical Drawing). The next Summer Term begins on the 24th of April. Throughout the Winter Session, besides various scientific researches, a great number of analyses have been undertaken in the different departments of the Laboratory for manufacturers of all kinds, in judicial cases, and in many branches of trade, mining, agriculture, and hygiene.

MEETINGS FOR THE WEEK.

TUESDAY, 17th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
— Photographic, 8.
— Pathological, 8.30.
WEDNESDAY, 18th.—Society of Arts, 8. "The Bahamas Sisal Industry," by Dr. D. Morris.
— Meteorological, 7.30.
— Microscopical, 8.

THURSDAY, 19th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "Masters of Modern Thought—III. Goethe," by The Rev. W. Barry, D.D.
— Society of Arts, 8. "The Great Landship at Gohna, in Gu-hwal," by J. H. Glass, C.I.E.
— Chemical, 8. "The Constitution of a New Organic Acid," by H. J. H. Fenton, M.A. "The Volume and Optical Relationships of the Monoclinic Series of Double Sulphates, $R_2M(SO_4)_2 \cdot 6H_2O$," by A. E. Tutton.
FRIDAY, 20th.—Royal Institution, 9. "Immunisation against Serpents' Venom and the Treatment of Snake-Bite with Antivenene," by Prof. T. R. Fraser, F.R.S.
— Quekett Club, 8.
SATURDAY, 21st.—Royal Institution, 3. "Light," by Lord Rayleigh, F.R.S., &c.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1895.

ON THE PASSAGE OF THE RÖNTGEN RAYS THROUGH LIQUIDS.

By MM. BLEUNARD and LABESSE.

In studying the influence which liquids may have on the passage of the Röntgen rays, it was necessary for us first to avoid the errors which might result from the transit of the rays through the vessel in which liquids have to be placed.

Glass is one of the substances which offer the greatest resistance to the passage of the Röntgen rays. On the other hand, vessels of wood or cardboard, covered with a layer of fatty matter, still oppose, in a certain degree, the passage of the rays. We have found that black paper, coated with suet, is, on the contrary, absolutely permeable. The sensitive plates wrapped up in ordinary black paper, upon which are arranged squares of paper coated with tallow, are acted upon by the rays with the utmost ease, without any trace indicating upon the plate the arrangement which has been given to the little trough of greased paper.

If we expose to the Röntgen rays a sensitive plate previously wrapped in black paper, upon which are placed equal depths of liquid in small paper troughs coated with tallow, the white spots obtained upon the sensitive paper must be exclusively due to the liquids forming the screens.

We have hitherto made only summary experiments, but some of the results already obtained present, we believe, a certain interest.

Water is easily traversed by the rays.

Solutions of potassium bromide, antimony chloride, potassium bichromate, offer a very considerable resistance to the passage of the Röntgen rays, whilst solutions of sodium bichromate and potassium permanganate are more easily traversed.

Colours seem to have no influence on the passage of the rays. Water coloured with various aniline colours offers no resistance.

Our intention is to pursue these researches.—*Comptes Rendus*, cxxii., p. 527.

OBSERVATIONS ON THE SUBJECT OF PHOTOGRAPHY THROUGH OPAQUE SUBSTANCES.

By A. D'ARSONVAL.

THE *savants* who have attempted to repeat the experiments of Le Bon are divided into two groups; some have obtained positive results, *e.g.*, Armagnac (of Bordeaux), Murat (of Havre), Braun (of Paris), &c.; others, like the Lumières, Londe, Monod, &c., have obtained no images.

I have myself repeated these experiments, and I think I have succeeded in finding the cause of the discrepancy among observers equally conscientious and skilful. Both are right: all depends on the experimental conditions. On operating like MM. Lumière, *i.e.*, on exposing to the solar rays a sensitive plate protected by a metal screen, I obtained no impression on the plate, even when the screen consists of a very slender plate of aluminium. The metal is therefore not traversed by the solar radiations, which seems to argue against the results obtained by Le Bon.

It is no longer the same if we interpose between the metallic plate and the solar rays a thick plate of glass,

like those which we find in the frames used for taking positives. Under such circumstances I have found in sufficient time, like M. Le Bon, a very feeble impression on the sensitive plate. If we place upon the metallic plate a piece of uranium glass, the impression on the sensitive plate is obtained more quickly. All glasses are not equally good. Those which give the best results are such as have a greenish yellow fluorescence if illuminated in the dark by the electric spark. I have further observed that it is the same with the phials yielding Röntgen's rays. We may substitute for the Crookes phial an incandescence lamp which is rendered fluorescent by connecting the filament with one of the poles of a coil of great frequency.

All the glow lamps which give a yellowish green fluorescence may be very well substituted for the Crookes phial; those, on the contrary, whose fluorescence is violet or bluish, give scarcely anything. I have also obtained a good result on using a single Geissler tube surrounded with a solution of fluoresceine.

In a word, it results from the above experiments that all the substances which emit fluorescent radiations of a yellowish green colour can act upon a photographic plate through opaque bodies.

The above contradictory results are very easily explained if we keep in mind the facts pointed out by Charles Henry, Nievenglowski, and especially by our colleague Henri Becquerel in the recent sessions. Fluorescent substances emit radiations having the properties of the X rays, in conformity with the hypothesis of our colleague Poincaré.

From all these facts it results that the rôle of the cathodic rays in Prof. Röntgen's experiments is limited to exciting the fluorescence of the special glass of which the Crookes phials are made.—*Comptes Rendus*, cxxii., p. 500.

ON DARK LIGHT: A REPLY TO CERTAIN CRITICISMS.

By GUSTAVE LE BON.

THE present paper is intended as a reply to the criticisms of MM. Lumière, who deny the existence of dark light; and to those of Zenger, who denies at once the dark light and the rays of Röntgen.

In reply to the critiques of MM. Lumière I point out that, even if we admit all their hypotheses, we should still find ourselves in presence of dark light. Light which is able, after being reflected at 93° three times successively, to pass between plates of glass and of metal, protected laterally by being fitted into a deep groove and compressed together by a weight of several kilos., will be totally invisible to the eye,—that is to say, precisely what I have called *dark light*.

We prove that it is invisible to the eye by placing ourselves in the conditions of our experiments. We form a pile of proofs, furnished behind and at their edges with black paper, and all our proofs are enclosed in such; we place then between them plates of metal, and submit the whole to a moderate pressure. If we view directly a luminous source along the edges of the system (even taking care to remain in darkness for a long time), we perceive absolutely no thread of light, although the source of illumination may be viewed directly without any of the successive radiations of which I have spoken.

When light penetrates into a case by any chink, the operator is at once made aware, by lines and veils, of a quite characteristic aspect. To obtain an image, even though very bad, the light must be admitted intentionally; but then the images produced are quite different from those obtained with dark light, as is proved by the specimens exhibited to the Academy.

The fact that MM. Lumière have obtained no images on pasting bands of black paper over all the edges of the

metallic plates is nothing surprising. According to the recognised laws of the distribution of static electricity, in conductive bodies the electricity does not traverse them, but is propagated by following their surface. I have supposed from some experiments that dark light is propagated in this manner. Whether it penetrates the plates or follows their outlines the result is the same. The slips of paper do not, doubtless, arrest the passage of the electricity, but since dark light, as I have indicated, is not entirely identifiable with electricity, it is quite admissible that the paper may act as an insulating body.

Various experimentalists have succeeded in obtaining results identical with mine. I mention among such M. Gaston Braun, a pupil of Prof. Eder, of Vienna, a son of the well-known Parisian photographer. As he has explained in a treatise recently published, he has adopted my arrangements, and has thus obtained reproductions of medals, of pieces of glass on which there had been traced designs, fishes, &c. He rightly remarks that the temperatures of the luminous source play a certain part.

I wrote to M. Braun to enquire the means of control which he had employed, especially for the reproduction of the medals. This is the substance of his reply:—No light stored up, since on performing the experiment in darkness after several hours no images were obtained. No lateral light through any fissure, since two plates were always side by side in the same frame, and the plate serving as a check never presented any veil. The plate of copper had exactly the dimensions of the frame, and was introduced with difficulty. No influence of the pressure of medals, since the same results were obtained on inverting a sensitive plate, *i.e.*, lacing the medals on the side of the glass.

As for the observations of Zenger relating to the non-existence of the X rays and of the dark light, they are perhaps better founded than the foregoing. His criticism is directed only to the interpretation of the results obtained. I see no impossibility in admitting that we have here to do with "phenomena of electric induction producing phosphorescence in the gelatin, and at the same time an electric discharge in the gelatin." It is very possible that the dark light does not act directly upon the sensitive plate, and is limited to rendering fluorescent the objects placed behind the metallic plates. We know that the experiments of Charles Henry seem to verify the hypothesis of M. Poincaré that fluorescent substances emit X rays. Thus would be explained M. Murat's reproduction of the subcutaneous regions of a ray behind a plate of metal. This experiment may be repeated on separating the sensitive layer from the animal by a slender film of transparent celluloid, to avoid chemical actions. The fluorescence becomes even visible to the eye in certain cases not yet determined. It would explain how we may with some animals obtain analogous results in darkness, as I have shown in my former paper.

But what results clearly from the above, and especially from the discrepancy of the results obtained by different experimentalists, is that all the conditions of the transit of light through opaque bodies are not yet determined. I hope soon to succeed in rendering these experiments much easier to repeat.—*Comptes Rendus*, cxxii., p. 522.

DETERMINATION OF ARSENIC.

By ARMAND GAUTIER.

In the *Comptes Rendus*, vol. cxxii., p. 390, appears a paper by MM. Engel and Bernard on a "Rapid Process for the Determination of Arsenic," in which, whilst admitting the accuracy of the process for the same purpose which I published in 1875 (*Bull. de la Soc. Chimique* and *Annales de Chimie et de Physique*, 5th Series, vol. viii., p. 384), they think their method preferable in any case on account of its rapidity.

If I admit that the interesting procedure of MM. Engel

and Bernard has this advantage (which I do not think) I will point out that the method which I have indicated alone permits us, by weighing the arsenical ring obtained, with the precautions laid down, to determine exactly minimal quantities of this element, even below 1 m.grm.

As a proof I quote merely some figures which I have obtained:—

Quantities of arsenic introduced into the Marsh apparatus.	Weight of the arsenical ring obtained.
0'0038	0'0037
0'0038	0'0037
0'0019	0'0018
0'00188	0'0018

The numbers agree almost as well when it is required to extract and determine minute quantities of arsenic mixed with animal matter.

Such quantities, we think, could scarcely be determined by the method of the authors quoted.

Now, the exact determination of the slightest traces of this element is the object indispensable to be obtained in industry, when it is requisite, *e.g.*, to estimate a metallurgical process, or the value of a metal in which the slightest traces of arsenic often modify all its physical properties, its colour, its hardness, its tenacity, &c. The volatilisation of arsenic and antimony in the gaseous state alone permits us to determine and separate exactly the minutest quantities of these substances in ores, metals, and alloys where they may exist merely in very minute proportions.

This method has been employed by Prof. van't Hoff in his researches on apparent exceptions to the law of Raoult when it is required to study mixtures of antimony and tin.

I must further remark that the method which I have published has the advantage of allowing arsenic and antimony, after being separated from the other metals, to be each determined in succession after the entire ring has been weighed.

I will, lastly, remark that this method alone enables us to determine arsenic as well in its mineral or organic combinations as when it exists in a latent state and in minimal quantities in the viscera of animals which have absorbed it during life.—*Comptes Rendus*, cxxii., p. 426.

EXTENSION OF NESSLER'S REACTION. DETECTION OF MERCURY AND IODIDES.

By G. DENIGÈS.

MERCURIAMMONIUM iodide-mercury oxide, which is formed by Nessler's reaction for the detection of ammonia, is readily obtained if we bring together a mercuric salt, ammonia, a caustic alkali, and potassium iodide, on condition that the salt last mentioned is not in excess, which would prevent the separation of the characteristic precipitate. For the production of this precipitate, the joint presence of the four substances just mentioned is necessary. If, in preparing the reagent, one of the four substances is omitted, the mixture can serve for the detection of the fourth substance, provided that other substances do not form a similar precipitate with the reagent. Experiments which I have made in this direction showed that the caustic alkali alone need be present in quantity, whilst mere traces of the other two are only needful for the detection of the fourth, by forming the mercuriammonium iodide mercuric oxide. It is here shown in what manner the Nessler reaction can serve for the detection of mercury and of iodides.

A.—Detection of Mercury.

1. *Simple Solutions of a Mercuric Salt.*—If it is desired to produce the precipitate in question with a mercuric salt, we put into a test-glass 2 c.c. of a 1 per cent solution

of mercuric chloride, add 1 c.c. of ammonia, and cause the precipitate thus produced to disappear by a suitable addition of potassium iodide. In general, 10 drops of a 20 per cent solution will suffice. In the detection of mercury by this method two cases are possible:—(a) The solution contains more than 0.5 grm. of mercury per litre, or (b) the solution is very dilute. In the former case the reaction is carried out as just indicated, with the precaution that the solution of iodide is added drop by drop in such a quantity as just suffices for re-dissolving the precipitate thrown down by the ammonia, or until a colouration just appears, when the lye is at once added and shaken up. In the second case we take 10 to 20 c.c. of the solution in question, add 1 c.c. ammonia, and the quantity of iodine solution just sufficient to re-dissolve the precipitate. If the mercuric solution contains only 1 to 2 centigram. per litre, one drop of the iodide solution is sufficient.

2. *Mercurial Compounds in general.*—If the substance is a liquid, we take 2 c.c.; if solid, we put a few centigrams into a test-glass, add, in either case, 1 c.c. hydrochloric acid and 0.5 nitric acid, and boil the mixture until only a few drops remain in the test-tube. The residue is taken up in 5 c.c. of water, filtered (if needful), and to the solution thus obtained there are added 2 c.c. ammonia, with 2 to 10 drops of a 20 per cent solution of potassium iodide, according to the quantity of the mercury present, and shake up. The liquid either remains clear, in which case the reaction ensues on the addition of caustic alkali, or there appears a white or coloured precipitate. If the precipitate is white, the reaction is not interfered with, and addition of caustic lye is sufficient to bring up the characteristic reaction. If the precipitate is coloured it is filtered off, and the filtrate is mixed with caustic lye. A colour may appear on the addition of potassium iodide, e.g., in presence of copper. In this case we dilute strongly, so that the colour appears less intense, and then add the caustic lye.

If carried out in this manner, the Nessler reaction may serve for the detection of the smallest quantities of mercury.

B.—Detection of Iodides.

If the substance under examination contains metals which are precipitated by the reagent, we use the filtrate from the ammonium sulphide precipitate. We filter, acidulate with hydrochloric acid, boil until the hydrogen sulphide is expelled, and supersaturate with ammonia. We add to the liquid a little caustic lye and a few drops of mercuric chloride, and shake up. If there appears a precipitate of a more or less deep red colour we may infer the presence of iodine. In the absence of iodine, the precipitate is white or slightly yellowish. We can prepare fresh for each time of using a mixture of 1 c.c. ammonia, $\frac{1}{2}$ c.c. soda-lye, and a few drops of solution of sublimate. If this mixture, which is yellowish, is brought in contact with the liquid obtained above, there appears, in presence of iodine, the characteristic precipitate of mercuric ammonium-iodide mercuric oxide. The reaction is very sensitive, and is applicable also for insoluble iodides.—*Chemiker Zeitung.*

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 126.)

CHAPTER VII.

CHEMICAL RESEARCHES ON CARBONATE, NITRATE, AND CHLORIDE OF STRONTIUM.

Barium, calcium, and strontium are closely associated both in the form of carbonate and of sulphate. Sodium is an accidental impurity, as are also the silicon, iron, and

manganese met with in native sulphates and carbonates of strontium. After a few preliminary experiments, I made in the following way some carbonate of strontium free from foreign bodies, which I then used for the spectroscopic study of strontium, as well as for making nitrate and chloride of this metal.

I took as raw material some chloride of strontium that I had previously purified from iron and manganese, by means of a solution of sulphide of strontium, and which had then been crystallised five times in succession, removing the mother-liquor each time, but which still contained barium, calcium, sodium, and silica.

The crystallised chloride was moistened, in a covered platinum retort, with a solution of pure chloride of ammonium, dried, and then heated till the greater part of the sal ammoniac was volatilised. The residue was dissolved in cold water, and the solution filtered to separate the now insoluble silica. The clear liquid was evaporated until it became solid, and the residue moistened afresh with a saturated solution of chloride of ammonium. It was dried at a low temperature, and the residue was once more heated till it freely gave off vapours of sal ammoniac. The chloride was re-dissolved in cold water, and the solution, though apparently clear, was again filtered. Finally, it was treated a third time with sal ammoniac, so as to make sure of having eliminated all the silica.

The solution of chloride after this third treatment was, after being passed through a purified filter-paper, added to five times its own volume of pure water, and poured into water containing 5 per cent of pure sulphuric acid. The sulphates of barium, calcium, and strontium, formed in a very dilute liquid, were flocculent. After six hours rest in a platinum vessel, the clear supernatant liquid was poured off and replaced by pure water, and the washing was continued until the decanted water no longer turned blue litmus-paper red.

The sulphates in the platinum vessel were then put to digest, cold, for sixteen hours, in an excess of a solution of sesqui-carbonate of ammonium, the mixture being stirred up from time to time; the insoluble mass was then washed and re-washed by decantation until the decanted water had no effect on red litmus-paper.

According to accepted theories, all the barium in the chloride of strontium used should be in the insoluble mass in the form of sulphate, whilst the sulphates of strontium and calcium should be converted into carbonates. To verify this I took about one-tenth of the whole, and, having put it into water, I added hydrochloric acid, drop by drop, taking care not to destroy all the carbonate mixed with the sulphate of barium. The chloride solution was clouded, and did not become clear on passing through a filter-paper. I had to leave it to settle, and this took a long time. After settling, the liquid which had deposited the carbonate dissolved by carbonic acid was filtered, and poured again into water containing sulphuric acid. The resulting sulphate, having been carefully washed by decantation, was treated cold with an excess of a solution of sesqui-carbonate of ammonium. After twelve hours action the mother-liquor, though clouded, was poured off, and the washing was continued until the decanted water, which was always slightly clouded, was entirely neutral to red litmus-paper. I then put the carbonate into water, and gradually added pure nitric acid, until nearly all the solids were dissolved. The nitrate solution, clouded by the carbonate in suspension, was left to settle, and the liquid was then decanted and filtered. I then acted on the remaining carbonate with a very dilute solution of nitric acid, and it was dissolved, forming a clear liquid.

Thus the barium was entirely in the form of sulphate in the residue left after reacting on a mixture of sulphates of barium, calcium, and strontium, when cold, by bicarbonate of ammonium. By taking care not to destroy all the carbonate in the mixture, one is certain not to dissolve the sulphate of barium.

Having ascertained this fact I converted, in the cold,

the bulk of the carbonates of strontium and calcium left in the platinum vessel into nitrates, taking care to leave at least one-tenth of the carbonates. The solution was very cloudy, and was not cleared by passing through a filter-paper. It was therefore left to settle and then filtered; this was a very slow process. I added to the clear liquid the solution of nitrate of strontium made before, and evaporated the whole to dryness in a covered platinum retort.

The nitrate when dried was in small crystals. I treated it with absolute alcohol, first cold, then at boiling-point. I continued the treatment until the nitrate of calcium was dissolved. I then put the residue into pure water; the solution not being clear, was filtered. It left a very slight white precipitate, consisting entirely of a mixture of carbonate of strontium and calcium, which was put to one side. The solution was again evaporated to dryness, and the nitrate, as a crystalline powder, was treated with absolute alcohol at boiling-point. It required to be dissolved in water, evaporated to dryness, and treated with boiling absolute alcohol *seven times* before all traces of nitrate of calcium—which was obstinately held by the nitrate of strontium—were completely eliminated. Before I tried it I had no idea of the difficulty I should have in getting entirely rid of the calcium. I only considered the calcium was completely eliminated when the residue, after evaporating an aqueous solution of nitrate of strontium to dryness, could be completely dissolved in boiling absolute alcohol. I was unable to detect the presence of calcium in this solution. As an experiment, I evaporated to dryness 100 c.c. of the alcoholic solution saturated at boiling-point, and I tested for calcium in the very small residue. For this purpose, I treated it first of all with a mixture of equal volumes of alcohol and anhydrous ether, and, having thus dissolved it, I evaporated the liquid in platinum; then I put the traces left from evaporating the liquid and the dried residue into an oxyhydrogen blowpipe, to examine the spectrum of the flame.

I have no hesitation in saying that the complete separation of the nitrates of calcium and strontium is the most difficult operation I know of. In addition, I tried to check the degree of purity of the nitrate, as I shall describe further on.

The nitrate of strontium, when freed from calcium salts by boiling alcohol, contained a notable amount of sodium, which could only be eliminated by converting the strontium into a carbonate. But nitrate is not suitable for preparing carbonate. When this salt is formed from nitrate it is always more or less granular, as is the case also with sulphate of barium, which retains the nitrate however the washings may be prolonged, and, although in the granular state the carbonate of strontium is easily washed, on the other hand it obstinately retains sodium.

I began therefore by converting the nitrate into carbonate, so that on pouring a dilute solution of this salt into an excess of a solution of sesqui-carbonate of ammonium, and after washing the granular carbonate as completely as possible, I could take it up by dilute hydrochloric acid.

Wishing to ascertain whether this chloride of strontium was quite free from calcium, I evaporated the whole solution to dryness in a platinum retort, and I treated the dehydrated residue, which was a crystalline powder, five times with boiling absolute alcohol, thus adopting M. Bunsen's method of separating calcium. I carefully examined for calcium, on the one hand, the chloride deposited by cooling the decanted boiling alcohol, and, on the other hand, the residue of evaporation of this alcohol after the deposition of the chloride. I was not able to detect, by spectrum analysis of an oxyhydrogen blowpipe flame turned on to these chlorides, any trace of the calcium spectrum, not even of its *green* line, which is never absent when chloride of strontium contains a weighable quantity of calcium.

Having got this negative result, I put all the chloride of strontium into water, and poured the dilute solution into

an excess of a solution of sesqui-carbonate of ammonium. When made in this way, carbonate of strontium is very tenuous; it makes water milky. I had to leave the liquid to settle, sheltered from draughts: this was a very slow process.

I washed the carbonate by decantation; it took about three months to complete the operation on about 200 grms. of carbonate. I only desisted when the decanted water ceased to cloud a dilute solution of nitrate of silver.

In this form carbonate of strontium, when put into a Bunsen flame on a platinum loop, coloured it very deep yellow, and showed the sodium spectrum for a very long time.

I could not use hydrochloric acid for dissolving it, and as for successive precipitations in sesqui-carbonate of ammonium years would not suffice to eliminate all the sodium capable of being thus removed. Besides, by working in this way, one would run the risk of introducing as much sodium from the air as the treatment would be able to eliminate from the carbonate. I therefore applied the method which succeeded so well in removing sodium from the carbonates of lithium and calcium precipitated under identical conditions; that is to say, I treated the carbonate of strontium with water charged with carbonic acid. With this object I put the carbonate into 4 litres of pure water, through which I slowly passed carbonic acid to saturation. After standing for a night, the liquid, though still clouded, was decanted into a platinum vessel and replaced by an equal volume of pure water. I again passed carbonic acid into it for twenty-four hours. I repeated the operation five times; then I put the carbonate into pure water, so long as the liquid, when settled, gave to a flame the slightest sodic characteristic.

The liquids containing carbonate of strontium with carbonic acid were separately boiled in platinum, in order to deposit the carbonate by setting free the acid. After boiling, the water from the first three treatments, after a moderate evaporation, sensibly coloured a flame yellow; the water from the fourth and fifth treatment did not give the sodic character to a flame. The carbonate of strontium deposited by the elimination of the carbonic acid, when put into a flame, gave it the sodium characteristics in every case, but less and less distinctly from the first to the fifth. In the third case the amount of sodium was so far reduced that, when heated in an oxyhydrogen blowpipe, oxide of strontium was formed completely free from sodium; this was not possible in the first two cases.

The bulk of the carbonate of strontium, which had been freed from sodium by means of water charged with carbonic acid, and then by boiling water, when put into a flame on a platinum loop, gave a sodic character temporarily, and not stronger than platinum which has been left for an hour in the air under a bell-jar after having been heated to redness.

After the experiment, the bulk of the carbonate was dried in the platinum vessel, protected from air dust; it was then kept under a bell-jar, in a covered platinum vessel. After being kept for several weeks, the carbonate gave a sodic character to flames, *just as though it had never been purified!*

I converted a small portion of carbonate which had been purified from sodium in an oxyhydrogen blowpipe into solid nitrate, and I mixed part of this salt with two parts of the same carbonate which had been previously freed from all sodic characteristics in an oxyhydrogen blowpipe. This mixture, when put into a conical cup, on a layer of pure oxide of strontium, enabled me to study the luminous spectrum of *coherent* oxide of strontium, much more easily than oxide made from carbonate alone in an oxyhydrogen blowpipe.

I prepared chloride of strontium by means of oxide made from the carbonate and pure chloride of ammonium. For this purpose, after having heated to whiteness a small crucible of pure platinum, I deposited on the bottom of the crucible a layer of pure chloride of ammo-

nium, made in platinum, and I poured on it a mixture of oxide of strontium and of the same chloride of ammonium. I covered the crucible and put it into a second platinum crucible, also covered; I then heated it, gently at first, and afterwards sufficiently to drive off all the excess chloride of ammonium, and yet not enough to melt the chloride.

When introduced into a Bunsen flame or an oxyhydrogen blowpipe, when quite fresh, the chloride gave them the sodic characteristics, but very slightly. Nevertheless the sodium line only disappeared completely when the chloride was almost entirely converted into basic oxychloride. Although the sodium spectrum appeared, there was a fundamental difference between the manner in which the very slightly hygroscopic chloride of strontium and the chlorides of lithium and calcium behaved, for the latter, as soon as they were made, gave persistent and strong signs of the presence of sodium.

Having met with great difficulties in preparing compounds of strontium which would not, on spectrum analysis, show any trace of the calcium lines, and especially of the green calcium line, I applied, through a friend, to a firm which prepared metals and salts for spectroscopic use. I must confess that, without exception, all the chloride of strontium thus supplied me contained calcium which I could not separate analytically. I make this statement, not to blame the chemical manufacturers, but to account for the errors into which persons are likely to fall who are obliged to procure commercially those chemicals they cannot prepare themselves, or of which they cannot verify analytically the absolute purity.

(To be continued).

THE COMPOSITION OF WATER. A SHORT BIBLIOGRAPHY.

By T. C. WARRINGTON, B.A.

THE following is a list of papers bearing on the determination of the ratio O : H, arranged in chronological order under the following headings:—

I. Determination of the relative densities of hydrogen and oxygen.

II. Determination of the ratio of the combining volumes of hydrogen and oxygen.

III. Gravimetric methods:—

a. The combination of weighed quantities of hydrogen and oxygen to form water (weighed in some cases).

b. The combination of a weighed quantity of oxygen with hydrogen to form a weighed quantity of water.

c. The combination of a weighed quantity of hydrogen with oxygen to form a weighed quantity of water.

d. Indirectly from the molecular weight of ammonium chloride.

IV. Critical and miscellaneous.

A full bibliography of the earlier papers on the composition of water and of the dispute as to the real discoverer, whether Cavendish, Watt, or Lavoisier, is to be found in the "Critical Account of Water Controversy, with Bibliography," Wilson's "Life of Cavendish," p. 269.

I. Determination of the Relative Densities of Hydrogen and Oxygen.

(1). 1841. DUMAS and BOUSSINGAULT.

"Recherches sur la véritable Constitution de l'Air Atmosphérique."

Ann. Chim. et Phys., (1841), [3], iii., p. 257.

Compt. Rend., (1841), xii., p. 1005 (abs.).

Erdm. J. pr. Chem., (1841), xxiv., p. 64 (translation).

Bibl. Univ., (1841), xxxiii., p. 363.

Liebig Ann., (1841), xl., p. 230.

Pogg. Ann., (1841), liii., p. 391.

During the course of an investigation on air, the density of oxygen relative to dry air is determined to be 1.1057 as the mean of three experiments.

(2). 1845. V. REGNAULT.

"Sur la Détermination de la Densité des Gaz."

Ann. Chim. et Phys., (1845), [3], xiv., p. 211; and xv., p. 512.

Erdm. J. pr. Chem., (1845), xxxv., p. 203.

Compt. Rend., (1845), xx., p. 975.

Pogg. Ann., (1845), lxv., p. 395.

(3). 1879. P. VON JOLLY.

"Die Veränderlichkeit in der Zusammensetzung der Atmosphärischen Luft."

München, Akad. Abhandl., (1880), xiii., (abt. ii.), p. 49.

Wied. Ann., (1879), vi., p. 520.

The densities of oxygen and nitrogen were determined.

(4). 1884. G. AGAMENNONE.

"Sulla Deformazione Prodotta in Vasi di Vetro da Pressioni interne."

Atti (Rend.) della Accad. dei Lincei, (1884-5), [4], i., pp. 665 and 699.

The author calculates the amount and coefficient of deformation of a glass vessel due to internal pressure.

(5). 1888. LORD RAYLEIGH.

"On the Relative Densities of Hydrogen and Oxygen." (Prel. Notice; read Feb., 1888).

Proc. R. S., (1887-8), xliii., p. 356.

Abs. J. C. S., (1888), liv., p. 643.

Chem. News, (1888), lvii., p. 73.

Beibl. Wied. Ann., (1888), xii., p. 411.

Regnault's method is used with additional precautions. Regnault's results are shown to be affected by the shrinkage of the vacuous globe, due to external pressure.

(6). 1888. J. M. CRAFTS.

"Sur une Correction à apporter aux Déterminations par Regnault du poids d'un Litre des Gaz Élémentaires." (Note).

Compt. Rend. (1888), cvi., p. 1662.

Ber., (1888), xxi., Ref. p. 503.

A globe of the same glass as that used by Regnault is employed to find the correction to be applied to Regnault's determination, arising from the shrinkage of vacuous globe. Cf. (5).

(7). 1889. J. P. COOKE.

"On a New Method of Determining Gas Densities."

Amer. Chem. J. (1889), xi., p. 509.

Proc. Amer. Acad. (1889), xxiv., [N.S. xvi.], p. 202.

Abs. J. C. S., (1890), lviii., p. 361.

Beibl. Wied. Ann., (1890), xiv., p. 213.

This method avoids shrinkage of vacuous balloon. The tare of the balloon is found by filling with CO₂, which is displaced by air into an absorption apparatus and weighed.

(8). 1890. J. JOLY.

"On a Method of Determining the Absolute Density of a Gas." (Read June, 1890).

Proc. R. Dublin Soc. (1888-90), vi., [N.S.], p. 534.

Phil. Mag., (1890), [5], xxx., p. 379. (Reprint).

Beibl. Wied. Ann., (1891), xv., p. 153.

The method consists in measuring the gas in one vessel, and compressing into a much smaller stout copper vessel which is used for weighing the gas. A specimen result for dry air is given.

(9). 1890. A. LEDUC.

"Sur la Densité de l'Azote et de l'Oxygène d'après Regnault, et la Composition de l'Air d'après Dumas et Boussingault." (Read Aug., 1890).

Compt. Rend., (1890), cxi., p. 262.
Journ. de Physique, (1891), [2], x., p. 37.
Beibl. Wied. Ann., (1891), xv., p. 1.

A comparison between the two sets of observations shows a want of agreement.

(10). 1890. ED. W. MORLEY.

"Ratio of the Densities of Oxygen and Hydrogen."

Proc. Amer. Ass., (1890), xxxix., p. 163.
Nature, (1890), xlii., p. 530.

The paper is an abstract, giving a sketch of the method, but no results. In the *Nature* report some figures are given.

(11). 1891. A. LEDUC.

"Sur les Densités de l'Oxygène, de l'Hydrogène, et de l'Azote."

Compt. Rend., (1891), cxiii., p. 186.
Abs. J. C. S., (1891), lx., p. 1416.
Beibl. Wied. Ann., (1892), xvi., p. 105.

Slight modification of Regnault's method.

(12). 1892. Lord RAYLEIGH.

"On the Relative Densities of Hydrogen and Oxygen."
II. (Read Feb., 1892).

Proc. R. S., (1891-2), l., p. 448.
Chem. News, (1892), lxx., pp. 200 and 206.
Abs. J. C. S., (1893), lxiv., II., p. 10.
Beibl. Wied. Ann., (1894), xviii., p. 2.
Nature, (1892), xli., p. 101.

Elaborate re determination with results, by a modification of Regnault's method.

(13). 1893. Lord RAYLEIGH.

"On the Densities of the Principal Gases." (Read Mar. 4, 1893).

Proc. R. S., (1893), liii., p. 134.
Chem. News, (1893), lxvii., pp. 183, 198, 211.
Amer. Jour. Sci., (1894), [3], xlvii., p. 234. (Abs.).
Abs. J. C. S., (1893), lxiv., II., p. 514.
Beibl. Wied. Ann., (1893), xvii., p. 685.

The densities of oxygen and hydrogen are determined and compared with those of other experimenters. Their bearing on the ratio O : H is discussed.

(14). 1893. A. LEDUC.

"Sur les Densités de quelques Gaz et la Composition de l'Eau." (Read May, 1893).

Compt. Rend., (1893) cxvi., p. 1248.
Beibl. Wied. Ann., (1893), xvii., p. 994.

The author discusses his own results with those of Rayleigh and Morley.

(15). 1893. A. LEDUC.

"Sur le Poids du litre d'Air Normal et la Densité des Gaz." (Read Dec., 1893).

Compt. Rend., (1893), cxvii., p. 1072.
Beibl. Wied. Ann., (1894), xviii., p. 489.

The accuracy of the method of determining gas-density discussed. Results given for air and nitrogen.

(To be continued.)

Properties of Metals extracted from their Amalgams.—M. Guntz.—Melted metals, as we know them, probably consist of very condensed molecules formed, with a liberation of heat, from their atomic state. This causes the properties of such metals not to agree with their thermic constants. Thus manganese, the oxidation heat of which (98.6 cal.) is close to that of the alkaline metals, is but little affected by the air when melted. These considerations explain the chemical activity of metals extracted from their amalgams at low temperatures.—*Comptes Rendus*, cxvii., No. 8.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 5th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. Alexander Simpson, Joseph John Bowley, Walter A. Voss, and William A. Bone were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Percival Jenkins, 30, St. John's Road, Clifton, Bristol; Tom Mitchell, Cemetery House, Shaw, near Oldham; Raymond St. George Ross, 30, Britannia Square, Worcester.

Of the following papers those marked * were read:—

*29. "The Explosion of Cyanogen." By H. B. DIXON M.A., F.R.S., E. H. STRANGE, B.Sc., and E. GRAHAM B.Sc.

Since it has been shown by previous investigators that cyanogen probably burns first to carbonic oxide, and secondly to carbon dioxide, both in ordinary flames and in the explosion wave, and since the burning of carbonic oxide to carbon dioxide appears to be generally conditioned by the presence of water vapour, it seemed of interest to investigate the course of the chemical changes occurring in the complete combustion of cyanogen.

The authors first measured the rate of explosion of cyanogen with an excess of oxygen. The conclusion drawn is that when cyanogen is exploded with its own volume of oxygen it burns directly to carbonic oxide; on adding a second volume of oxygen to the mixture, carbonic oxide is formed in the wave front, and the heated carbonic oxide and oxygen combine behind the wave-front; on adding more oxygen the formation of carbon dioxide is sufficiently rapid to affect the velocity of the wave itself. When one volume of cyanogen is exploded with four volumes of oxygen, the rate is 5 per cent faster than the rate calculated on the supposition that the cyanogen is only burning to carbonic oxide in the wave-front. The formation of carbon dioxide, although without influence on the velocity of the wave in the faster explosions, is found to exert an influence in the slower explosions.

In order to study the intensity and duration of the flame following the explosion wave, photographs were taken of the jets of flame projected from the ends of long tubes filled with the explosive mixtures of cyanogen and oxygen. Since the wave travels faster than sound in the unburnt gas the wave-front must reach the end of the tube before any other disturbance can be propagated through the gas; the jet of flame which is driven from the tube must accordingly be part of the column of burning gases following in the wake of the wave. When cyanogen is burnt with its own volume of oxygen to carbonic oxide, the intensity of the explosion is very great, but only a very slight jet of flame is projected from the tube. The length of column of highly heated gases must be short. But when cyanogen is burnt with twice its volume of oxygen to carbon dioxide the explosion is less intense, but the jet of flame projected from the tube is long and of considerable brightness. The column of highly heated gases must therefore be long. If the extra oxygen is inert in the wave-front it accounts for the superior brilliancy of the unimpeded reaction $C_2N_2 + O_2 = 2CO + N_2$ over the impeded reaction $C_2N_2 + 2O_2 = 2CO + O_2 + N_2$, and if the formation of carbon dioxide mainly occurs behind the wave, it accounts for the brightness of the jet of still burning gases thrown from the tube in the second case.

To obtain a direct record of the intensity and length of flame in the two cases, the explosion wave was photographed on a very rapidly moving film as it passed a short window in a long tube. The sensitive film was fixed round a light iron drum driven by a high speed electric

motor. Two tubes, each provided with a window, were fixed side by side, one being filled with one mixture, the second with the other. The gases being fired simultaneously, the two flames were photographed on the same film. On developing the film in a long trough each image received precisely the same treatment, and one could be compared with the other.

The front of the flame in all cases was sharply defined, but the rear of the flame dies away in a tail which gradually thins out. When cyanogen is exploded with its own volume of oxygen, an intense image of the window is produced, only slightly drawn out by the revolution of the drum, followed by a faint and short tail. When, however, cyanogen is exploded with twice its volume of oxygen, the image is not so bright and there is no abrupt fall in intensity; the tail is much brighter and longer. These photographs accord with the view that cyanogen burns first to carbonic oxide, and that the formation of carbon dioxide is a secondary action.

Photographs were then taken with the same apparatus of the flames produced by mixtures of cyanogen with two vols. of oxygen (1) well dried, and (2) moist. No difference could be detected in the images of the flames. Water-vapour, therefore, does not seem to affect the reaction between oxygen and the just-formed carbonic oxide. Similar photographs of the flames produced in mixtures of carbonic oxide and oxygen in the dry and moist state showed a marked difference; in the presence of steam the flame is intenser and shorter.

*30. "On the Mode of Formation of Carbon Dioxide in the Burning of Carbon Compounds." By H. B. DIXON, M.A., F.R.S.

Assuming that in the combustion of carbon compounds the carbon burns first to carbonic oxide, the author discusses the views that have been advanced concerning the function of steam in promoting the union of carbonic oxide and oxygen.

Professor Armstrong considers that the moisture acts as an electrolyte, and that chemical change only takes place when carbonic oxide, steam, and oxygen are in contact. The chief difficulty in this theory is to account for the great velocity with which the explosion wave is propagated through a damp mixture of carbonic oxide and oxygen. In gaseous mixtures the rate of explosion approximates to the rate of the forward movement of the reacting molecules, i.e., the wave is transmitted like sound from molecule to molecule. According to the electrolytic theory, the chemical change could only occur on the simultaneous collision of at least three molecules; yet the explosion wave is propagated in carbonic oxide, steam, and oxygen at a rate of 1738 metres per second. In the explosion of cyanogen, carbon dioxide is formed without the intervention of steam. This theory, which has the advantage of including a number of cognate phenomena, seems better suited to explain reactions at ordinary temperatures than those occurring in the explosion wave.

A similar difficulty occurs in Professor J. J. Thomson's theory, according to which the steam, by forming liquid particles, produces dissociation of the oxygen molecules, and thus facilitates the oxidation of the carbonic oxide. It is hard to understand how steam, which is far below the saturation point at ordinary temperatures, can be condensed in the explosion wave.

Mendeleeff considers that carbonic oxide cannot combine directly with oxygen because all combination between gases takes place according to the law of equal volumes. Carbonic oxide and steam react in equal volumes, and therefore the change begins by the carbonic oxide taking the oxygen from the steam. The liberated hydrogen unites with its own volume of oxygen to form hydrogen peroxide, and this in turn reacts with its own volume of carbonic oxide to form carbon dioxide and water. The spark will not, however, kindle a mixture of dried carbonic oxide and nitrous oxide (mixed in equal volumes), but the addition of a trace of steam renders the mixture explosive.

Lothar Meyer and Beketoff attribute the influence of the steam to the fact that the direct action of carbonic oxide on oxygen requires a very high temperature, whereas carbonic oxide decomposes steam much more readily. But although it may be true that steam facilitates the oxidation of carbonic oxide on account of the low temperature of the reaction, this does not account for the non-union of carbonic oxide and oxygen at the intensely high temperature produced in the wave-front in the explosion of cyanogen.

The author shows that a dried mixture of carbonic oxide and ozonised oxygen is not inflamed by the spark; here the resistance cannot be attributed to the stability of oxygen.

The author has repeated Beketoff's experiment of exploding together a mixture of cyanogen, carbonic oxide, and oxygen in the dry state. With quantities of cyanogen below 12 per cent the flame causes an incomplete combustion of the carbonic oxide. The same results were obtained when carbon bisulphide was substituted for cyanogen. The more intense the exciting flame, the larger was the amount of carbonic oxide burnt.

The dissociation of carbon dioxide, held by Bunsen and by Deville to limit the combustion of carbonic oxide and oxygen, may be the reason why carbonic oxide and oxygen do not unite in the wave-front, but can combine as the gases cool down behind the wave. The reaction between steam and carbonic oxide gives out little heat, so carbonic acid might be formed indirectly, and the liberated hydrogen might re-form steam, which could exist at a temperature at which carbonic acid would be broken up. The union of dry carbonic oxide and oxygen, without flame, on the surface of platinum, may be due partly to the power of the metal to conduct away heat.

The dissociation theory explains some of the facts observed concerning the combustion of carbonic oxide, but probably some other cause exists which limits the union of carbonic oxide and oxygen at lower temperatures.

The Röntgen rays do not appear to make a dried mixture of carbonic oxide and oxygen inflammable.

*31. "On the Explosion of Chlorine Peroxide." By H. B. DIXON, M.A., F.R.S., and J. A. HARKER, D.Sc.

The decomposition by shock of endothermic compounds, discovered by M. Berthelot, and the explosion of carbon bisulphide vapour described by Dr. Thorpe, led the authors to determine whether a true explosion-wave was transmitted through these compounds. It was found, however, that when a charge of fulminate was fired in a steel bomb attached to a long tube filled with cyanogen or acetylene, the detonation was not transmitted through the gas in the tube except for a short distance. With carbon bisulphide the flame extended for some distance, but gradually died out. M. Maquenne has recently obtained similar results.

A mixture of chlorine peroxide and oxygen (with a trace of chlorine) was prepared by warming potassium chlorate with sulphuric acid. The gases were passed up through a long glass tube, 33 ft. long, inclined at an angle of 30°. When the tube was full, "bridge-pieces" were clamped on at each end. The explosion was started by igniting a mixture of hydrogen and oxygen in one bridge-piece. The explosion-wave set up in this was communicated to the chlorine peroxide. By making the explosion break a silver bridge (coated with paraffin) at each end of the tube, the rate of the explosion was determined on the electric chronograph. A sample of the gas for analysis was collected at the end of the tube.

In two experiments the following results were obtained:—

	Composition of mixture.	Rate of explosion in metres per second.
1.	$\left\{ \begin{array}{l} \text{ClO}_2 \dots \dots 53.5 \\ \text{O}_2 \dots \dots 46.5 \end{array} \right\} \dots \dots \dots$	1065
2.	$\left\{ \begin{array}{l} \text{ClO}_2 \dots \dots 64.0 \\ \text{O}_2 \dots \dots 36.0 \end{array} \right\} \dots \dots \dots$	1126

It would appear, therefore, that a true explosion-wave is propagated through chlorine peroxide.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, March 13th, 1896.

Prof. CAREY FOSTER, Vice-President, in the Chair.

Mr. J. H. REEVES read a paper on "*An Addition to the Wheatstone's Bridge for the Determination of Low Resistances.*"

The piece of apparatus described can be used for measuring the resistance of metre lengths of wires of low resistance, the only additional apparatus required being a sensitive galvanometer, a Post-Office form of resistance-box, and a metre bridge. It differs from the ordinary Kelvin bridge in that, instead of balancing by varying the length of the standard wire between the two contacts, the distance between these contacts is maintained constant, as is also the length of the wire which is being measured, and balance is obtained by altering other resistances in the network. The author has made a number of tests which show that by his arrangement the resistance of metre lengths of copper wires between the limits of No. 22 S.W.G. and a standard cable of 7 No. 16's can be determined with an accuracy of 0.1 per cent.

Mr. REEVES also read a "*Note on the Exact Value of Matthiessen's Standard.*"

Prof. A. GRAY (communicated) said that the author had in his arrangement combined the fixed standard employed in Matthiessen and Hocking's modification of the ordinary bridge with the greater celerity of working arising from the smaller number of operations to be performed when the Kelvin bridge is used. Prof. Gray thinks that he, and probably others, have used a method similar to that of Mr. Reeves, but that the paper is of great utility since it shows how time may be saved and existing apparatus utilised.

Prof. AYRTON said that the advantage of the method described lay in the fact that it was independent of the resistances at the contacts. In Carey Foster's method, however, the coils had to be interchanged, and inaccuracy might be introduced owing to the varying resistance of the mercury contacts. Unless the mercury cups and the copper plates at the bottom were cleaned every day, and the contacts re-amalgamated, the resistance of the mercury cups was very variable. With regard to the question of Matthiessen's standard, it is to be remembered that the specific conductivity of copper has been steadily increasing. This increase was particularly noticeable in the copper prepared by the Elmore process, where, during the deposition of the metal, an agate burnisher is kept continually passing over the surface. Fitzpatrick had explained the rise in conductivity of copper by supposing that the density of the copper now supplied was greater than that of the copper used by Matthiessen, and this explanation seemed quite satisfactory. Mr. Reeves' experiments, however, have conclusively shown that this is not the true explanation; it was now possible to obtain copper in large quantity having a conductivity of 103 on Matthiessen's scale.

The Chairman (Prof. CAREY FOSTER) explained how, when using his method, the accuracy of the result depends not on the elimination of the small resistances at the mercury cups, but on the constancy of these resistances. Matthiessen and Dr. Russell found that the specific gravity of copper was apt to be low, on account of the presence of dissolved oxide, and they were the first to pass hydrogen gas through the molten metal to remove this oxide.

Mr. APPLEYARD gave a simple diagrammatic sketch of the author's arrangement, and also pointed out that

better results would probably be obtained with a galvanometer of 1 or 2 ohms resistance.

Mr. CAMPBELL said that it ought to be definitely settled whether Matthiessen's standard was the conductivity per unit volume or per unit mass. Since copper was always bought by weight, he, as a practical man, strongly advocated the adoption of the mass conductivity; further, in this case the measurement of the specific gravity would be avoided.

Mr. Reeves replied.

A communication, by Herr PULJ, "*On Kathode Rays*" was read by the Secretary.

Herr Pulj exhibited some Röntgen photographs taken by means of a form of Crookes tube which he had described in a memoir published in 1889. With this tube he has succeeded in obtaining impressions with exposures of only two seconds.

Herr Pulj considers that the particles of matter torn from the kathode, which convey negative electrostatic charges, by impact on the glass walls or on screens, equalise their electric charges, and in this process call forth not merely a disturbance of the material molecules, but also of their ether envelopes. Each portion of the glass or screen bombarded by the kathode stream becomes the starting-point of ether waves, which, according to their oscillation period and oscillation character, are either visible rays (phosphorescence) or invisible Röntgen rays. The oscillations of the invisible rays may take place in the longitudinal direction, but no convincing argument has up to now been brought forward to support this view.

The Secretary also read a "*Note on Permeability to Röntgen Rays,*" by Messrs. ACKROYD and KNOWLES.

The authors have exposed a plate on which a number of pieces of metal, oxides, and sulphates were placed to the Röntgen rays in order to see whether the permeability of bodies to these rays depends on the atomic or molecular weight of the body. In each case it was found that the opacity increased with the molecular weight.

Mr. BLAKESLEY said that he considered the Röntgen rays to be the propagation of electrostatic strain through space. With reference to the non-refrangibility of these rays, he had observed in one of the photographs exhibited by Mr. Swinton a dark line at the edge of the shadow of a wooden pencil, which might have been due to the refraction of the rays by the wood. Mr. Blakesley has, however, found that this line is due to the varnish on the pencil. Some Röntgen photographs of quartz and ebonite rods not only did not exhibit these dark lines, but there was a very slight indication of a bright line just on the edge of the shadow, which would indicate that the refraction of these rays was less in the rods than in the surrounding medium.

Mr. EDSER exhibited some photographs taken with Mr. Jackson's form of tube, in which a concave kathode is employed. Mr. Edser said that the whole of the tube on the kathode side of the anode plate phosphoresced, so that the Röntgen rays seem to partake of the character of diffused light.

Prof. AYRTON said Mr. Jackson had found that the kathode rays form a parallel beam, and do not first come to a focus and then again spread out.

The CHAIRMAN said some observations made by Mr. Porter agreed with those of Mr. Edser.

Mr. BLAKESLEY described the tube used by Pulj, in which a mica screen coated with green calcium sulphide is placed between the kathode and the anode.

Mr. GARDNER said that there seemed to be some confusion, for when a concave kathode is employed, the kathode rays are brought to a focus and then again diverge. The phosphorescence on the inside of the glass had been shown by Lenard to be due to electricity travelling round the inside surface of the glass.

Mr. PIDGEON asked if any one had tried the effect of mounting the photographic film on a metal plate.

The CHAIRMAN said that Captain Abney had found that if the film was mounted on a ferrotype plate no action took place.

Prof. PERRY said he, for one, was of opinion that the Röntgen rays were undulatory. Prof. Larmor had given an explanation which seems to agree with the observed facts. This explanation supposes that the intermolecular spaces respond to vibrations of a certain frequency. The reason no refraction or diffraction effects had been observed was probably because of the extreme smallness of the wave-length of the undulation.

After some further remarks by some of the members the Society adjourned till March 27th.

NOTICES OF BOOKS.

Food and Sanitation. Vol. VII., No. 180, February 29, 1896.

THE foreign relations of *Food and Sanitation* appear to be in a state of tension. It has a *casus belli* against the *Lancet*, dating as far back as 1893, relating to Valentine's "meat juice," and another concerning the *Lancet's* commission on lamps and mineral oils. There is also a delicate innuendo on "blackmail and its results." With these disputes we have certainly no call to interfere.

We must, however, agree with *Food and Sanitation* in pronouncing 73° F. not a safe flashing-point for mineral oils, especially in view of the late serious accidents.

In the leader entitled "The *Lancet* on its Defence" we notice passing commendation of a certain "Sewage Purification Company." Now we can understand international copyright, international patent-right, or even international arbitration; but by what logical *tour de force* a process for sewage treatment can be called "international" is inconceivable.

But *Food and Sanitation* is at war also with the *Daily Chronicle*, with the National Health Society, and Mr. Ernest Hart. Who is wrong and who is right in these differences of opinion we cannot examine. Our contemporary deserves, however, the support of the public for its outspoken position as regards the adulteration of food, a subject on which British law is lamentably weak.

Aluminium. Manchester: The Aluminium Supply Company, 38, Victoria Buildings.

WE have here a small book setting forth the properties and applications of a metal which is deservedly claiming an increased share of attention. The metal aluminium is here called sometimes *aluminium* and sometimes *alum*, an unpleasant *alias* which is here considered necessary in these days of hurry and scurry. Because the electric power utilised in the production of aluminium by means of energy derived from the Niagara Falls, the author thinks he may be pardoned for introducing into a mechanical work a few views of the Falls—a somewhat threadbare addition.

We find here an account of the composition and forms of the "alum" supplied by the Pittsburgh Reduction Company under the patents of Charles M. Hall. The percentage of actual aluminium in the alum is stated as 99.75 to 99.25 per cent, though they have in stock metal at 99.90 per cent. The author speaks of the resistance of the metal to oxidation and corrosion. Its usual impurities are said to be silicon and iron. Of sodium, which has of late been detected in samples of aluminium prepared electrolytically, and which seriously interferes with the useful properties of the metal, nothing is said. The author speaks of the strength of the metal, its solubility, its galvanic action, and place in the electro-chemical series. Here we find the very necessary caution that "alum" exposed to liquids should not come in contact with any other metal, as the metal is then liable to be

impaired by electric action. A similar caution must apply to alloys and to impurities of the metal. The applications of "alum," actual and prospective, are described without any exaggeration.

The difficulty of soldering aluminium has not been overlooked, but it is stated that the Pittsburgh Company supply a special solder and flux which greatly overcome the difficulties.

We regret to note that no instructions are given for the analysis of commercial samples of aluminium. Information of such a kind would have been much more to the purpose than tables of the areas and circumferences of circles which have no special reference to aluminium, and which, as they fill up quite one-tenth of the book, can scarcely be regarded as other than "padding."

Intensity Coils, how Made and how Used: also Electric Light, Telephone, Phonograph, &c. By "DYER." Seventeenth Edition. London: Perken, Son, and Rayment, 99, Hatton Garden. Pp. 138.

THIS is a clearly written and abundantly illustrated little volume. From the mere fact that it has gone through seventeen editions we may infer how widely it has been appreciated.

To the amateur, and to the incipient electrician who aims at learning by experiment, we know of no book which we could recommend in preference.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., No. 8, February 24, 1896.

Radiations emitted by Phosphorescence.—Henri Becquerel.—In a former Session, Ch. Henry announced that phosphorescent zinc sulphide interposed in the track of rays emanating from a Crookes tube augments the intensity of the radiations traversing aluminium. On the other hand, M. Nievenglowski has observed that commercial phosphorescent calcium sulphide emits radiations which traverse opaque bodies. This fact extends to various phosphorescent substances, and especially to uranium salts, the phosphorescence of which has a very brief duration. I have been able to perform the following experiment with double uranium and potassium phosphate:—We enclose a *Lumière* photographic plate (gelatino-bromide) in two folds of very thick paper, so that the plate does not become shaded on exposure to the sun for a day. We place on the outside of the sheet of paper a plate of the phosphorescent substance, and expose the whole to the sun for several hours. When we then develop the photographic plate, we find that the silhouette of the phosphorescent substance appears in black on the proof. If we interpose a coin between the phosphorescent substance and the paper we see its image appear on the proof. We may repeat the same experiment by interposing a thin plate of glass between the phosphorescent substance and the paper, which excludes the possibility of a chemical action due to vapours which might emanate from the substance heated by the rays of the sun.

Manganese Carbide.—Henri Moissan.—The carbide, CMn_3 , discovered by Troost and Hautefeuille may be produced at temperatures between 1500° and 3000°. When pure, it decomposes water at ordinary temperatures, giving a mixture of methane and hydrogen in equal parts.

Nickel and Cobalt Boride.—Henri Moissan.—The nickel and cobalt borides, BoNi and BoCo , are easily ob-

tained in a crystalline state at 1200°. These novel compounds have properties analogous to those of iron boride, previously described. They enable us to introduce boron into such metals as iron, since at a high temperature boron and silicon expel carbon from melted cast iron.

Determination of Arsenic.—Armand Gautier.—(See p. 134).

Process used to Confer Immunity against the Bites of Serpents.—D'Abbadie (from documents furnished by Sr. de Serpa Pinto).—The patient is inoculated with the venom of the Alcatifa, a venomous serpent of East Africa. After the operation the person takes an oath never to kill a venomous serpent.

Transformation of Dextro-camphoric Acid into Dextro-camphor. Partial Synthesis of Camphor.—A. Haller.—The author has no doubt of the identity of the camphor derived from camphoric acid with ordinary camphor.

Volumetric Analysis of a Mixture of Chlorides, Hypochlorides, and Chlorates.—Ad. Carnot.

Analysis of a Mixture of Chlorides, Chlorates, and Perchlorates.—Ad. Carnot.—These two papers will be inserted as soon as practicable.

Production of Röntgen's Silhouettes.—Ch. V. Zenger.—In the abstract of my paper inserted in the *Comptes Rendus* it was not mentioned that the successful proofs sent by me had been obtained in the laboratory of the Slavic Polytechnicum, of Prague, between the 11th and the 22nd of January. They were taken by Domalip, professor of electrotechnics at this school, in concert with Brozet, demonstrator of physics. The interesting point is that Domalip has obtained electric images on the plate by means of plates of copper, brass, zinc, lead, and steel. This is, in my opinion, the proof that there is here merely a phenomenon of electric induction producing phosphorescence of the gelatin, and at the same time an electric discharge in the gelatin; and, lastly, the fluorescence of the ambient air, and, as in case of the dark discharge, of the electricity. In my opinion, these are the three agents which determine the decomposition of the silver salts in the sensitive layer. There are no special radiations, no X rays, and no dark light.

Action of the X Rays upon the Diamond.—Abel Buguet and Albert Gascard.—Already inserted.

Cause of the Invisibility of Röntgen's Rays.—MM. Darioux and De Rochas.—This and the five following papers will be inserted in full.

Röntgen's Rays.—Georges Meslin.

Some Properties of Röntgen's X Rays.—H. Dufour.

Emission of Röntgen's Rays by Tubes containing a Fluorescent Substance.—M. Piltchikoff.

Certain Properties of the Dark Light.—Gustave le Bon.—(See p. 121).

Photography through Opaque Bodies.—A. and L. Lumière.

Action of some Hydrogen Compounds upon Sulphuryl Chloride.—A. Besson.—Not suitable for abridgement.

Yield of various Volatile Wood Oils in Charcoal: Methylic Alcohol and Acetic Acid.—Ernest Barillot.—This memoir requires the accompanying figure.

Temperature of the Sparks produced by Uranium.—M. Chesneau.—These sparks ignite, not merely coal-gas (much more easily than sparks of iron), but also wicks of cotton saturated with ethylic alcohol at 90 per cent, benzene, and petroleum essence. The author proposes to utilise this property for lighting lamps.

New Method of Forming Nitro-prussides.—C. Marie and R. Marquis.—The authors' experiments show that we may pass from hydroferrocyanic acid to nitroprussic acid by the elimination of a mol. of hydrocyanic

acid and substituting a NO group and an atom of hydrogen.

Crystalline Ammoniacal Chromous Carbonate.—Georges Baugé.—The author has obtained, by general methods, a new compound, $\text{CO}_3\text{Cr} \cdot \text{CO}_3(\text{NH}_4)_2\text{H}_2\text{O}$. This is the first double ammoniacal salt of chromous oxide.

Veratrylamine.—Ch. Moureu.—This compound is easily obtained by acting upon veratrol with ordinary nitric acid.

Thermochemical Study of Orthochlorobenzoic Acid and some of its Derivatives.—Paul Rivals.—Not suitable for abstraction.

Conversion of the Solution of Liquid Formaldehyd into Vapours for Disinfection.—A. Trillat.—The volatilisation of liquid formaldehyd can be effected without the introduction of deleterious gases, such as carbon monoxide, effecting the destruction of the most various pathogenic microbia.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements after Easter:—Professor James Sully, of University College, London, three lectures on "Child-Study and Education"; Mr. C. Vernon Boys, three lectures on "Ripples in Air and on Water"; Professor T. G. Bonney, two lectures on the "Building and Sculpture of Western Europe" (the Tyndall Lectures); Professor Dewar, three lectures on "Recent Chemical Progress"; Mr. W. Gowland, three lectures on the "Art of Working Metals in Japan"; Dr. Robert Munro, two lectures on "Lake Dwellings"; Professor W. B. Richmond, R.A., three lectures on the "Vault of the Sixtine Chapel"; Mr. F. Corder, Curator of the Royal Academy of Music, three lectures on "Three Emotional Composers"—Berlioz, Wagner, Liszt (with musical illustrations); Mr. E. A. Wallis Budge, of the British Museum, two lectures on "The Moral and Religious Literature of Ancient Egypt." The Friday evening meetings will be resumed on April 17th, when a discourse will be given by M. G. Lippmann, on "Colour Photography"; succeeding discourses will probably be given by Professor G. V. Poore, Colonel H. Watkin, C.B., Professor Silvanus P. Thompson, Professor J. A. Ewing, Professor J. A. Fleming, and other gentlemen.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Medical, 8.30.

TUESDAY, 24th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.

— Medical and Chirurgical, 8.30.

— Institute of Civil Engineers, 8.

— Photographic, 8.

— Society of Arts, 8. "The Colonies and the Supply of Dairy Produce and Products of Petite Culture," by Charles R. Valentine.

WEDNESDAY, 25th.—Society of Arts, 8. "Our Food Supply, as affected by the Farming of the Future," by Prof. James Long.

— British Astronomical, 5.

— Geological, 8.

THURSDAY, 26th.—Royal Institution, 3. "Masters of Modern Thought—IV. Spinoza," by The Rev. W. Barry, D.D.

— Institute of Electrical Engineers, 8.

— Society of Arts, 8. "Kashmir—its People and its Products," by Walter R. Lawrence, C.I.E.

— Chemical, 8. (Anniversary Meeting). President's Address, Election of Officers and Council.

FRIDAY, 27th.—Royal Institution, 9. "New Researches on Liquid Air," by Prof. Dewar, F.R.S.

— Physical, 5.

SATURDAY, 28th.—Royal Institution, 3. "Light," by Lord Rayleigh, F.R.S., &c.

THE CHEMICAL NEWS.

VOL. LXXIII., No. 1896.

ON SOME SPECIMENS OF GLASS EXPOSED TO THE ACTION OF THE X RAYS.

By V. CHABAUD.

Six specimens of glass of different compositions were cut to the thickness of $\frac{1}{10}$ m.m. Of each specimen I made three rectangular plates. Upon a card of the dimension $\frac{1}{10}$ m.m. I cemented six small plates of platinum of $\frac{1}{20}$ m.m. in thickness and 2 m.m. in width.

Upon each platinum plate I arranged two plates of the same specimen, so as to have at the middle two thicknesses. Transversely in the midst, and perpendicular to the two former, I placed the third plate. This arrangement enabled me to have at the centre three thicknesses, i.e. 1.35 m.m., at each side of the centre two thicknesses—that is, $\frac{1}{10}$ of a m.m.—and at the four extremities a single thickness, or $\frac{1}{20}$.

This arrangement was placed on a case of wood containing the photographic plate. The whole covered with a black paper to prevent the direct action of the light emitted by the Crookes tube and of the diffused light of the piece upon the glasses submitted to experiment. The samples of glass themselves had been kept in darkness for two days.

The Crookes tube was placed with its side at 20 c.m. from the surface of the case. The current which passed into the induction coil was furnished by three accumulators; one ammeter placed in the circuit indicated 5 amperes.

The duration of the experiment was sixty minutes.

The Crookes tube was covered outwardly up to the level of the plane passing by the surface of the kathode with a tin paper—the arrangement of Hurmuzescu, in order to augment the yield of the tube.

The six specimens submitted to experiment were the following:—

- | | | |
|----------------------------|----|---|
| Fluorescence (water-green) | A. | Glass with a base of soda, potash, and lime. |
| " (blue) .. | B. | Crystal. |
| " (pale water-green) .. | C. | Ternary glass, with a base of soda, potash, and lime. |
| " (yellowish green) .. | D. | German glass. |
| | E. | Light uranium glass. |
| | F. | Dark uranium glass. |

The proof, when developed, enabled us to see that:—

1. The three glasses A, C, D are the most permeable to the Röntgen rays, and this permeability is very great.
2. Crystal is refractory.
3. The two specimens of uranium glass are traversed with more difficulty than the three glasses A, B, and D.
4. The dark uranium glass was more refractory than the pale uranium glass.

The opacity of crystal glass is easily explained by the presence of lead. The slight transparency of uranium glass can be explained only by admitting the presence of foreign substances, possibly arsenic.

We may also find in these results an explanation of the fact already noticed, that glasses with a blue fluorescence do not give the Röntgen rays, or only to a slight extent.

This may be because the wall of the tube opposes the passage of these rays. The seat of the emission of the Röntgen rays would therefore be in the interior of the tube.—*Comptes Rendus*, cxxii., p. 603.

ON THE USE OF ARTIFICIAL HEXAGONAL BLENDE AS A SUBSTITUTE FOR THE CROOKES PHIALS.

By M. TROOST.

ARTIFICIAL blende, which we obtained in concert with Henri Sainte-Claire Deville, in 1861, in the form of hexagonal prisms, transparent, colourless, or slightly yellowish, is capable, as it is known, of acquiring a very fine fluorescence under the influence of the solar light, or of the magnesium flame.

I thought that specimens of these crystals permanent in air and light, and easy to prepare by the procedures which we have laid down (*Comptes Rendus*, lii., p. 983; and *Annales de Chimie et de Physique*, Series 4, vol. vi., p. 120), might serve as substitutes for Crookes phials in a great number of experiments which are being made at present on the X rays.

To satisfy myself, I placed a silver gelatino-bromide plate in one of the opaque cardboard boxes which MM. Lumière use for preserving their sensitised plates. I then placed upon this plate, covered with paper, certain perforated metallic objects, a watch-chain, &c., and the box was closed with its opaque cover.

Under these conditions the photographic plate was secure from the action of ordinary light. The specimen of crystals (hexagonal) of blende was fixed by means of plugs of wadding in a metal box closed with a plate of glass applied on the cardboard box containing the photographic plate and the metallic objects.

As the sun did not shine during the experiments, the hexagonal blende was rendered phosphorescent by the combustion of a slip of magnesium, and the whole was kept in darkness. The plate, when developed afterwards by the ordinary procedures, gave a very fine negative, with which I afterwards obtained the very strong negative which I submit to the view of the Academy.

These results, which confirm the hypothesis of our colleague, H. Poincaré, and the experiments recently made by various savants, and especially by our colleague H. Becquerel, by Nievenglowski, and Charles Henry, enable us to substitute, if needful, by a simple apparatus, easy to manage, and of an unlimited permanence, the phials of Crookes which require the use of electric currents and a Ruhmkorff coil. These phials are also readily frangible, and are rendered useless by a current too prolonged or slightly too intense.

They require, further, the absolute immobility of the electric apparatus and of the object to be photographed during the whole time of exposure, which limits its applications, especially for surgical diagnosis in living beings.

The metal box containing the artificial hexagonal blende, on the contrary, may be fixed, as also the silver gelatino-bromide plate, by a suitable bandage to the hand, e.g., to be photographed without interfering with the displacement of the rest of the body.—*Comptes Rendus*, cxxii., p. 564.

"Argon and Newton—a Realisation" is the title of a new volume from the pen of Lieut.-Colonel W. Sedgwick, of the Royal Engineers. It is published by W. B. Whittingham and Co. (Ltd.), of "The Charterhouse Press." It is a book for Students of Chemistry Problems. (286 pages, price 7s. 6d.)

THE RÔLE OF THE VARIOUS FORMS OF ENERGY IN PHOTOGRAPHY THROUGH OPAQUE BODIES.

By R. COLSON.

SINCE the discovery of the X rays very numerous experiments have been performed in the search for new means of acting on photographic plates through opaque bodies. Hence there results at present a certain confusion which we can remedy only by a very definite classification of the various effects produced on the sensitive surface of the different forms of energy. In the present paper I purpose summarising the rules to be formulated according to known results, and according to my own observations.

These forms of energy may be classified as:—Mechanical, chemical, thermic, and luminous; there is perhaps room to add the electric form when we have determined its direct influence without the transformations which carry back its effects to one of the foregoing. We must further classify separately the X rays until we have decided upon their real nature.

1. The mechanical action consists in pressure or friction exerted by hard substances in contact with the plate, and shown, on development, by black marks.

2. It is easy to distinguish a chemical action; in every case we may foresee the result according to the nature of the substances present. The contact of a substance capable of producing blackness by the reduction or transformation of a compound of silver acts especially if moisture intervenes. For instance, the humidity which arises from heating a proof in contact with the plate may contain variable proportions of the developer or of hyposulphite. But a chemical influence may also be produced in dryness. I will mention, as an instance, the contact of dry insect, which, as I have found, de-sensitises the stratum by the oxidation of the organic matter, and economises the light on development. It is the same whenever this substance is oxidised.

3. Dry heat is capable of determining the preliminary work which the revealer completes by blackening the proof.

If the plate is wrapped in several thicknesses of black paper, or placed near a source of heat (e.g., an arc lamp), we find that certain parts of the surface are covered and remain light in a revealer which veils the other parts.

I apply on a plate in a camera obscura a card in which I have cut out letters, and expose it for five minutes to watery vapour at about 35°; the gelatin shows the letters in relief in the places which have least undergone the influence of the steam, and in hollows in those which had been most exposed to steam and to heat. The veil of development leaves the letters clear, those especially which were hollow.

A plate is first treated with steam, as in the foregoing experiment, and then heated to 40° for a minute. The letters of moist gelatin undergo incipient fusion, form a decided hollow on drying, and still remain lighter in the revealer.

I lay on a plate three pieces of silver of 2 frcs., carefully cleansed to prevent any chemical action; the whole is wrapped in black paper and kept for two hours on the marble of a "calorifère" at about 40°, with a weight of 1 kilo. upon one of the pieces. On developing, this piece comes out light with a black margin caused by the pressure. The other pieces give nothing.

Thus, in fine, on those parts of the plates rendered moist by the steam given off by the wrapping, or by the vapour escaping from the gelatin, and which is imprisoned on its surface by a body in contact, the heat produces a modification which leaves these parts clear in the revealer; the effect is heightened by the rise of temperature.

This influence is important, for it tends to manifest itself when we employ the direct rays of the sun or the

light of burning substances; that is, in a great number of cases.

4. The ultra-red radiations, if sufficiently intense, act upon the plate like the visible radiations.

For the visible radiations we must take account of the property which the plate possesses to accumulate successive effects, whilst the eye is saturated in the fraction of a second. Behind a board of pine-wood, of 5 m.m. in thickness, I applied a Lumière plate (blue), protected and maintained by four sheets of black paper glued to the wood. After an exposure of eight hours to diffused daylight, I obtained a good proof, showing the structure of the wood and giving a negative of a proof on paper interposed between the plate and the board; tin paper was slightly permeated, and black paper not at all. I satisfied myself that under these conditions of lighting it would be necessary to reduce the thickness to less than 3 m.m. for the eye accustomed to darkness to perceive the light through. The luminous rays may, therefore, in time act upon the plate in a manner appreciable through bodies which we call opaque.

Cornu has shown, in 1880, when studying the reflective power of various metals, that it is possible to observe by fluorescence the very refrangible ultra-violet radiations through a plate of silver deposited chemically and sufficiently thick to arrest the rays of the sun; the transparency is especially observable near the ray R. M. de Chardonnet has utilised this property of silver for photographing objects apparently invisible, and has found that if these rays are not visible it is because they are absorbed by the media of the eye. It is probable that the rays traverse a great number of substances called opaque. But whether they act directly, or by the intervention of phosphorescent or fluorescent bodies, their effect is still shown by the blackening of the plate on development.

We must here include the effects which spring from an incomplete protection of the sensitive surface during the experiment.

5. It is easy to recognise the X rays on wrapping the plate in black paper, and on placing on the track a thick card or a board with glass and iron, which give a light spot on the black ground due to the rays.

These indications enable us to analyse that which passes in each case, and to analyse the true causes of the phenomena observed.—*Comptes Rendus*, cxxii., p. 598.

A SMALL NOVELTY IN PHOTOGRAPHS WITH THE RÖNTGEN RAYS.

THE photographs obtained with the X rays which have hitherto been published, have doubtless all been produced by the image of the shadow of the transilluminated object upon a sensitive plate, from which copies were thus obtained in the ordinary manner. On transillumination, the parts of the object totally or partially impervious to the X rays produced no impression upon the plate; hence, on the developed plate these parts appeared colourless and transparent, and on the copies black (bones, rings, metallic objects, &c.). The copy also displayed a reflected image of the object taken; hence, e.g., a right-hand appeared as a left, &c. By occasion of a number of experiments which I instituted, Dr. Heseckel suggested that instead of a photographic plate I should use the silver bromide paper which has been introduced into trade. The experiment was very successful. With the silver bromide paper I obtained direct shadow images of the object, the right-hand of the image remained the right-hand, and the portions of the object impervious to the X rays now appeared white, or in the shades of greyish white to grey, which I believe brings out the details better than the former method of operating. The thought suggested itself whether several superimposed silver bromide papers would give simultaneously shadow images of the same object. I placed the superimposed papers and a photo-

graphic plate under a narcotised frog, and illuminated the whole with the X rays. I obtained thirteen shadow images of the same frog without fig. 1 and fig. 13 differing from each other in sharpness or details. In like manner, I have photographed in series the human hand, fishes, and other objects, all with the same result. This new method of operating, besides the advantage that it yields real shadow images of the transilluminated object, is decidedly cheaper, and can be effected in less time than with the circuitous method of the photographic plate. I believe that the medical practitioner who seeks to combine with the photograph surgical operation will be able to make use of this procedure with advantage.

In connection with this subject, Prof. Luntz and I have attempted to ascertain whether X rays are present in the electric arc light. If this were the fact, a sensitive plate placed in a closed case would after development display the shadow image of a piece of metal or a thick glass prism which had been superimposed during the exposure. After exposures of respectively thirty and ninety minutes the result on the sensitive plate was negative.—*Chemiker Zeitung*, February 26, 1896.

ON A NEW AND ABUNDANT SOURCE OF THE RARE OXIDES OF THORIUM, CERIUM, YTTRIUM, LANTHANUM, DIDYMIUM, AND ZIRCONIUM.

By Dr. T. L. PHIPSON.

It has been known for a long time that most of the minerals containing the rare oxides of the metals thorium, cerium, yttrium, lanthanum, didymium, and zirconium are attacked by acids; and I have been able to prove that these minerals, or at least the oxides which characterise them, are more or less widely dispersed through the Norwegian granites. Probably this will be found to be the case with granites from other localities, but my present remarks apply only to the former.

A good many years ago I extracted considerable amounts of zirconium from the zircon-syenite of Norway, of which I brought various specimens to England in 1860, all of which had been seen and verified by the celebrated geologist Dumont, of Liège. In this case, however, the oxide of zirconium was extracted by the usual process, and it served me later (*Comptes Rendus*, 1865) to obtain the metal zirconium by the action of magnesium. I may take this opportunity of stating that M. Moissan has recently been kind enough to point out in the *Comptes Rendus* that this was the first time the metal zirconium had ever been obtained in a state of purity, and he adopted the process in his new researches on that metal.

Being convinced that the rare oxides above named must be widely dispersed throughout the granite rocks of the regions where their minerals are found, I made a number of experiments, not only with the zircon-syenite, but with the ordinary Norwegian granite ("crust" or "tender") which is used along with "Blue Guernsey" and "Aberdeen" for the kerb-stones which pave the road in which is situated my new Casa Mia Laboratory, at Putney. This granite has flesh-coloured and white (or greenish white) felspar, with black mica. The latter, however, becomes quite white after the acid treatment to which I am going to refer.

About 15 to 20 grms. of the rock, reduced to a very fine powder, are heated with pure hydrochloric acid, just as if it were a sample of ironstone. After the acid has been kept gently boiling for about an hour, water is added, and, after depositing, the clear liquid is carefully decanted off through a filter. Another lot of pure acid is then poured over the residue, and it is boiled again in the same manner. A few crystals of chlorate of potash are added to ensure that all the iron is in the state of peroxide. The residue may be digested for two or three days with

strong sulphuric acid, afterwards heated, diluted, and filtered, &c.; but the extra yield of oxides is very small, and the hydrochloric acid treatment alone appears to extract all that is worth having.

The diluted hydrochloric acid liquid is saturated with ammonia until only a very small amount of free hydrochloric acid remains, and then an excess (about a gm.) of crystals of oxalic acid is thrown in and dissolved by stirring. The liquid, having stood for twenty-four hours, is decanted from the precipitate, and the small quantity of free hydrochloric acid is exactly saturated with ammonia; it is then allowed to deposit its oxalates again in presence of an excess of oxalic acid. In this manner the rare oxides are classified into two categories: those whose oxalates resist a little free hydrochloric acid, and those which only resist free oxalic acid.

The oxalates, being dried and calcined, yield a mixture of the rare oxides and carbonates of the metals mentioned above, much cheaper than by employing the expensive minerals thorite, orangite, cerite, gadolinite, monazite, pyrochlor, eudialite, &c., usually required for this purpose. The oxides named have been tolerably well characterised in the products obtained as above; but I can give no idea of their respective quantities more than to say that ceric oxide, yttrium, and didymium, with lanthanum, appear the most prominent, whilst thorium and zirconia were somewhat less abundant. Very slight quantities of some metal (or metals) precipitable by HS (black precipitate in acid liquid) are present also. By the above process I obtained 1.93, or nearly 2 per cent, of rare oxides and carbonates. This yield shows that there are, dispersed through the Norwegian granite (independently of the zircon-syenite), hundreds of tons of the rare oxides which can be promptly and easily extracted, and to some extent separated by the process I have just described.

The calcined oxalates from the liquor containing a little free hydrochloric acid yield a brick-coloured mixture of oxides and carbonates, which contains cerium oxide with zirconia or thorium (or both) amounting to 0.33 per cent; this yields to hydrochloric acid 0.03 of an oxide (yttria or lanthana), giving a very bulky oxalate. The oxalates from the liquor containing only free oxalic acid yield, on calcination, a greenish brown, or brown, mixture of oxides and carbonates, which colour is not due to manganese (which is not precipitated in the above circumstances), and amounting to 1.60 per cent. This product also contains much cerium oxide, with didymium, lanthanum, and yttria.

The Casa Mia Laboratory, Putney.

THE COMPOSITION OF WATER. A SHORT BIBLIOGRAPHY.

By T. C. WARRINGTON, B.A.

(Continued from p. 138).

II. Determination of the Ratio of the Combining Volumes of Hydrogen and Oxygen.

(16). 1805. HUMBOLDT and GAY-LUSSAC.

"Expériences sur les moyens Eudiométriques et sur la Proportion des Principes Constituans de l'Atmosphère."

Jour. de Physique, (1805), lx., p. 129.

Silb. Ann., (1805), xx., pp. 38 and 139. (Translation).

In searching for the best eudiometric means of estimating N and O in air, the authors decide on the use of Volta's method by explosion of the two gases. They find that two volumes of hydrogen explode with one of oxygen to form water.

(17). 1805. CHAPTAL and BERTHOLLET.

"Rapport sur un Mémoire présenté par MM. Humboldt et Gay-Lussac."

Ann. Chim. et Phys., (1805), liii., p. 239.
Resumé of above paper (16), with comments.

(18). 1887. A. SCOTT.

"On the Composition of Water by Volume."

Proc. R. S., (1887), xlii., p. 396.
Chem. News, (1887), lvi., p. 173.
Abs. J. C. S., (1888), liv., p. 411.
Beibl. Wied. Ann., (1887), xi., p. 743.

Both gases are measured in the same vessel, a separate vessel being used for explosion. The residue is analysed.

(19). 1887. A. SCOTT.

"On the Composition of Water by Volume."

Rep. of Brit. Assoc., (1887), p. 668.

Abstract of results of experiments.

(20). 1888. E. W. MORLEY.

"On the Determination of the Atomic Weight of Oxygen." (Dated Nov. 27, 1887).

Amer. Chem. J. (1888), x., p. 21.
Abs. J. C. S., (1888), liv., p. 649.
Beibl. Wied. Ann., (1888), xii., p. 731.

The paper is preliminary and describes the method adopted, part of which consists in the determination of the actual combining volumes of hydrogen and oxygen. No results are given. The method of Scott is criticised (18).

(21). 1888. SYDNEY YOUNG.

"The Composition of Water."

Nature (Feb. 23, 1888), xxxvii., p. 390.

Letter, attempting to establish a relation between the impurity in the gases used and the calculated ratio of volumes in Scott's results, with an attempt to fix the true value of the ratio.

(22). 1888. S. YOUNG.

"The Composition of Water."

Nature (March 1, 1888), xxxvii., p. 416.

Letter, supplementing previous one in the light of Scott's additional results.

(23). 1888. A. SCOTT.

"The Composition of Water by Volume."

Nature (March 8, 1888), xxxvii., p. 439.

Letter, giving some results and a cause of error, viz., use of lubricant.

(24). 1890. E. W. MORLEY.

"Determination of Volumetric Composition of Water." (Abstract).

Proc. Amer. Ass. (1890), xxxix., p. 161.
Nature, (1890), xlii., p. 530.

The method is briefly described and some results are given.

(25). 1891. E. W. MORLEY.

"The Volumetric Composition of Water."

Amer. Jour. Sci., (1891), [3], xli., pp. 220 and 276.
Chem. News, (1891), lxiii., pp. 218, 229, 239.
Abs. J. C. S., (1891), lx., p. 976.
Beibl. Wied. Ann., (1891), xv., p. 679.

Previous work is reviewed with copious references; a new method is described and results are tabulated.

(26). 1891. W. A. R.

"The Composition of Water."

Chem. News, (1891), lxiii., p. 236.

Letter, criticising Morley (24).

(27). 1892. A. LEDUC.

"Application de la Mesure des Densités à la Détermination du Poids Atomique de l'Oxygène." (Note).

Compt. Rend., (1892), cxv., p. 311.
Chem. News, (1892), lxvi., p. 149.
Abs. J. C. S., (1892), lxii., p. 1388.
Beibl. Wied. Ann., (1893), xvii., p. 1.

The author uses his previous determinations of the densities of the gases (11), and determines their relative volumes by electrolysis.

(28). 1893. A. SCOTT.

"On Composition of Water by Volume."

Phil. Trans., (1893), clxxxiv., p. 543.
Proc. R. S., (1893), liii., p. 130. (Abstract).
Abs. J. C. S., (1893), lxiv., II., p. 515.
Chem. News, (1893), lxvii., p. 243.
Beibl. Wied. Ann., (1893), xvii., p. 686.
Zeit. Phys. Chem., (1893), xi., p. 832.

Complete account of author's work.

(To be continued.)

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 29TH, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, March 10th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Feb. 1st to Feb. 29th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined one was recorded as "clear but dull," the remainder being clear, bright, and well filtered.

The rainfall at Oxford during the month has been 0.36 inch, as against 1.76 inches, the average for the past 30 years; this shows a deficiency of 1.40 inches, as compared with the average.

The rainfall in the Thames Valley during the months of January and February shows a deficiency of nearly 3 inches on the average of 30 years. This extraordinary dryness has practically reduced the Thames supply to natural springs. As a necessary consequence the unfiltered Thames water shows now quite an exceptional degree of purity. The increase of rainfall, which must in all probability occur soon, will no doubt bring the River back to its normal condition.

During the past month the water supplied to the Metropolis was of first-rate quality.

Our bacteriological examinations for the month of Feb-

ruary resulted in the following numbers of Colonies being found per cubic centimetre :—

	Colonies per c.c.
Thames water, unfiltered	1453
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	46
Ditto ditto lowest	14
Ditto ditto .. (12 samples) mean	26
New River water, unfiltered	1368
New River water, from the Company's clear water well	29
River Lea water, unfiltered	1109
River Lea water from the East London Com- pany's clear water well	28

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 137).

CHAPTER VIII.

THE CHARACTERISTICS GIVEN TO FLAMES, AND TO AN ELECTRIC SPARK, DISCHARGE, OR ARC, BY STRONTIUM COMPOUNDS.

The Luminous Spectra of Strontium.—In this research my object was to ascertain whether a strontium compound could be formed which, when brought to the highest possible temperature in a flame, or an electric spark, discharge, or arc, would not show, on spectrum analysis, conclusive traces of the spectra of sodium, potassium, lithium, calcium, or barium.

To obtain oxide of strontium, I started with purified carbonate, as is described in the preceding chapter. I must warn any one who takes up this subject, that he will have very great difficulty in getting carbonate of strontium completely freed from carbonate of calcium. Besides, the variations found by my illustrious master, Dumas, during his work on the atomic weight of strontium, show conclusively how extremely difficult it is to entirely separate the barium and calcium which are so intimately associated with chloride, nitrate, and carbonate of strontium. The necessity for effecting a complete separation is much greater when, under the conditions mentioned, the flame spectrum of strontium shows the green lines which indicate the presence of either calcium or barium in the compound submitted to analysis.

The conversion of carbonate into hydroxide of strontium was performed in the same manner as that of carbonate into oxide of calcium. The decarbonisation, although slower, can be completely effected if care is taken to use an oxyhydrogen blowpipe with an excess of hydrogen, and to heat it with that part of the flame whose temperature is high enough to melt platinum.

By proceeding thus, even although all possible precautions have been taken to protect the very purest carbonate of strontium from atmospheric sodium dust, as soon as it is made red hot the oxyhydrogen blowpipe flame turns yellow, and the sodium line appears very strongly when the carbonate has been long in contact with air. Still, by exercising great care and attention, after heating it for a time which varies between fifteen and twenty minutes, and after volatilising at least half the hydroxide produced, the sodium may be so far eliminated that the blowpipe flame will show, on spectrum analysis, only fugitive traces of the sodium line.

I made a great many experiments with the object of ascertaining whether I could see the strontium spectrum

without the sodium line, but I only succeeded twice. This happened when I was working in pure air, or rather when spectrum analysis of an oxyhydrogen blowpipe showed no trace of the sodium line, and, in order to preserve the relative purity of the air, I took care the previous evening to effect the decarbonisation, and to eliminate sodium from the hydroxide of strontium I was about to experiment with, and I also had the benches and the floor thoroughly washed at the same time.

I must add that the elimination of sodium so far as to show the sodium line no stronger than it usually appears in an oxyhydrogen blowpipe in air, is a very delicate operation, and that one frequently succeeds only in burning a hole in the concave platinum plate holding the fused hydroxide.

Although there is this difficulty, yet, by putting the hydroxide, as free as possible from sodium, into a conical cup in another concave sheet of recently heated platinum, and by fusing it in a hydrogen blowpipe to get rid of sodium as far as possible, a stage is reached at which a splendid strontium spectrum is seen without a trace of the sodium line, provided that the air at that very moment does not show the latter spectrum; in the other case, the sodium line appears almost as distinctly in the strontium spectrum as in the oxyhydrogen blowpipe. When the air happened to be pure—a state which only occurred twice during the six months occupied by my research on strontium—careful observation enabled me to note variations in the appearance and disappearance of the sodium line.

If, after having freed the outer layers of fused hydroxide of strontium from sodium, in an oxyhydrogen blowpipe, one volatilises it, and so exposes deeper layers, the sodium line reappears, only to disappear once more. I succeeded one day in causing these alternations, which gradually lessened in intensity, when volatilising several grms. of pure hydroxide of strontium in an oxy-coal-gas blowpipe.

This hydroxide freed from sodium, when left for twelve hours in air under a bell jar, and then introduced into an oxyhydrogen blowpipe, showed the sodium spectrum in just the same way as platinum, silver, oxide of lithium, and oxide of calcium, which had been in contact with air.

The flame of an oxyhydrogen blowpipe assumed a deep purplish red colour when projected on to pure fused hydroxide. At a temperature near the fusing-point of iridium, the purple colour was replaced by a deeper blue than that of incandescent hydrogen.

For instance, on introducing hydroxide into the inner cone of an oxyhydrogen blowpipe, by means of a small cone of pure carbon, the point of contact becomes deep blue, and the rest of the flame a purplish colour.

Fused hydroxide, and more especially its vapour, attacks platinum, colouring it black. Its vapour makes air pungent, but less so than the vapour of oxide of calcium. When left undisturbed, strontium settles in air more rapidly than calcium and lithium. Although I have frequently made heavy fumes of oxide of strontium, after three or four hours, I was unable to detect the least trace of a strontium spectrum in an oxyhydrogen blowpipe. After calcium and lithium had been freely volatilised,—as I had to do during my researches,—the air had to be left undisturbed for at least eighteen hours before an air spectrum could be shown without disclosing their presence. Oxide of lithium is so volatile that, several hours after I finished my work, burners in the next room to the one I was working in still showed a very distinct lithium colour.

The Flame Spectrum of Strontium.—In his remarkable work on spectrum analysis, Roscoe gives such a correct illustration of the spectrum of chloride of strontium, as measured by Messrs. Bunsen and Kirchhoff, that no description can improve upon it. When seen in a hydrogen or coal-gas flame, the spectrum consists of six red bands, one orange band, clearly separated if the slit is narrow enough, on a dark background, and one blue line.

Oxide or hydroxide of strontium, when introduced into an oxyhydrogen or oxy-coal-gas blowpipe, at a temper-

ature below the fusing-point of platinum, forms a spectrum like that described above. But on making a spectrum analysis of a blowpipe flame heated up to the fusing-point of platinum, and making the slit sufficiently narrow, the six red bands and the orange band are resolved into *diffuse and nebulous* lines; that is to say, they lack the sharpness of the blue line, and more especially of the lines formed by means of an electric spark charged with anhydrous chloride or hydrate of strontium. The spectra of the sharp bands are always similar.

It is possible to completely volatilise pure oxide or hydroxide of strontium in an oxyhydrogen or oxy-coal-gas blowpipe, without seeing any other lines on the dark background, by taking care to analyse only that part of the strontium flame in which the hydrogen is not incandescent, and which above all does not show a continuous spectrum.

When a part nearer to the inner cone, and most especially the inner cone itself, of a flame charged with strontium is analysed, the spectrum becomes modified; there are then seen, with oxyhydrogen gas, a dark band from A nearly to D, marked by the seven red bands and a strong, diffuse, orange line, and a green tinge from D to F. This tinge shows *three*, and sometimes *four*, green lines. The same thing is seen when using an oxy-coal-gas blowpipe. The colour of these green lines is quite distinct from that of either calcium or barium lines, and is the same as that of the green lines in the spectrum of the inner luminous cone of oxy-coal-gas itself, as I described in the first chapter.*

However much I tried to see the two violet-blue lines observed by M. Bunsen at 136.5 and 150.5 on his spectroscopic in the spark spectrum of chloride, I could not find them. I found, on the other hand, that the introduction of hydroxide of strontium into the inner luminous cone of an oxy-coal-gas blowpipe immediately showed the two blue bands and the blue line shown by spectrum analysis of this oxy-coal-gas cone. In this case the spectrum consisted of six diffuse red lines and a very strong orange line, on a dark background and characteristic of strontium, of two green bands on a luminous background, consisting of three and sometimes four sharp lines fading off from left to right, and finally of the blue strontium line on a dark background.

In order to find out, on the one hand, whether the green lines seen really belong to the flame spectrum of hydroxide of strontium, and, on the other hand, whether the absence of the two new violet-blue lines at 136.5 and 150.5, seen by M. Bunsen in the spark spectrum, are due to my method of investigation,—that is, to the *oxyhydrogen blowpipe*,—or to a difference in the compound, I examined the spectrum of chloride of strontium both in an oxyhydrogen and in an oxy-coal-gas blowpipe, and also in an electric spark, discharge, and arc.

An oxyhydrogen blowpipe in which the hydrogen is not incandescent, when impinged on to chloride of strontium, shows, on spectrum analysis, the same spectrum as that seen with hydrogen or a Bunsen lamp burning in air. On sufficiently closing the slit, the bands become nebulous lines. The bands and lines appear to undulate in the same way as those due to chloride of calcium heated in the same way. This apparent undulation lasts until the chloride is completely dissociated.

Anhydrous chloride of strontium, when put, by means of a small cone of pure carbon, into that part of an oxyhydrogen blowpipe where rhodium and iridium are fused, forms a flame *white in the centre, blue in the middle, and deep red round the edge*, in which spectrum analysis shows the six red bands almost merged into one. These bands only appear as nebulous lines after the chloride is dissociated and transformed into hydroxide or oxychloride of strontium.

At the same time that the red bands are seen merged together, there are also visible the strong orange line quite distinct, and *three or four* green lines fading off from

right to left, and a single blue line. Every attempt to cause TO APPEAR, or at least TO SEE, at the same time the two pale violet-blue lines, seen by M. Bunsen in the electric spectrum, failed.

I got a different result when analysing a spark or a discharge from an induction-coil, with or without a condenser, charged with chloride, or with the hydroxide formed by dissociating chloride. For these researches I used in succession a Steinheil spectroscopic, a large instrument by M. Hilger, fitted alternately with three or six prisms of Iceland spar, a spectroscopic with two half-prisms of quartz, made by M. Hilger for M. Depaire, and a direct-vision spectroscopic that Messrs. Liveing and Dewar kindly had made for me by M. Hilger.

During my observations, I used at first platinum balls and then small cones of pure carbon, coated either with chloride, oxychloride, or hydroxide of strontium. These compounds, when volatilised in an induction-spark or discharge, imparted a deep blue colour to them, and showed long and complete lines on spectrum analysis. Having found that the number and brightness of the air lines varied with the space between the coated balls, I replaced them by pure platinum balls fixed at half a c.m. apart, using coils which gave sparks of five, fifteen, and forty-five c.m. length.

After having found that, with this invariable distance, the number and position of the air lines were constant, I wetted the balls by means of a fine platinum wire loop, coated with a fluid paste of crystallised and dissolved chloride of strontium, quite free from calcium and barium, or I simply coated them with a saturated solution of hydroxide of strontium made from chloride or carbonate dissociated in an oxyhydrogen blowpipe. I thus found that, after deducting the air lines, the spectrum of a weak or strong induction spark and of a discharge, charged with chloride or hydroxide, was the same as the spectrum of chloride in a spark as described by Bunsen in Table VI., No. 8, of his "Spektal Analytische Untersuchungen," including in it the last two pale violet-blue lines, tabulated at 136.5 and 150.25 divisions on his spectroscopic, corresponding to 126.5 and 138.5 on my Steinheil spectroscopic.

Spectrum analysis of the discharge from a Ruhmkorff coil, giving sparks 45 c.m. long, between platinum balls or pure carbon cones coated with chloride or hydroxide of strontium, or the same balls or cones wetted with a saturated solution of these compounds, showed, together with the numerous and inevitable air lines, exactly the same lines that were seen with a spark, either weak or strong.

These investigations have convinced me that there is no advantage in increasing the electrical power of a spark. As far as the number of lines is concerned, there is no difference between the spectrum of chloride or hydroxide of strontium with a five, fifteen, or forty-five c.m. spark, when they are reduced to a half c.m. by moving the coated balls or cones nearer together. But the luminosity and colour of the lines, and more especially their visibility, increase with the electric power. The strontium spectrum does not alter after the characteristic strontium lines in a spark have appeared, and the difficulty of observing and fatigue of the eyes are accentuated by the appearance of a greater number of air lines.

In an electric arc formed by thirty of the largest-sized Bunsen cells, between pure carbon electrodes in contact and coated with fused chloride or hydroxide, the same lines are visible as those seen in the discharge, but with this difference—that in the arc spectrum of strontium these air lines, which make an examination of the discharge spectrum so difficult and fatiguing, do not appear.

Bunsen found the following bands and lines to be common to the flame and electric spectra:—

Flame Spectrum.		Electric Spectrum.	
Bunsen.	Stas.	Bunsen.	Stas.
36 to 37	37 to 38	36 to 37	36 to 38
39	40	39	40
47	47	47	47
105.5	98.5	105.5	98.5

* See CHEMICAL NEWS, vol. lxxii., p. 226.

I found the same bands and lines to be common to both spectra. I found besides that, beyond the fusing-point of platinum, hydroxide from carbonate and chloride of strontium has, in its flame spectrum, three, and sometimes four, green lines common to the spectrum of chloride and hydroxide in the spark and arc. These green lines are quite absent from the flame spectrum when the hydrogen is not incandescent.

The strong band in the flame spectrum between 31 and 34 on Bunsen's spectroscopic, only appeared in my research in a rudimentary form in the electric spectrum, however intense the spark or arc might be, and, on the other hand, I was unable to cause in an oxyhydrogen spectrum the appearance of the line at 89.75, mentioned by Bunsen in the spark spectrum, and frequently seen by myself in the same spectrum, both with chloride and hydroxide of strontium at 85 divisions on my Steinheil spectroscopic.

The flame spectrum of strontium varies with the temperature. Its appearance is different in hydrogen burning in air and in hydrogen highly incandescent. Both these spectra are typical, but can be changed from one to the other by altering the temperature.

I utterly failed to find either of them in the electric spectrum. The flame spectrum, whether complete or incomplete, preserved its characteristic appearance, whatever I did. Certain of its bands, perhaps, might be resolved almost into lines, but the edges of these lines remained diffuse; the orange band persisted longest.

The electric spectrum of chloride and hydroxide of strontium has some lines in common with the flame spectrum of the same bodies. This spectrum cannot be changed into either of the flame spectra of strontium.

My researches tend to prove the existence of three distinct types of strontium spectra. The second type of flame spectrum appears to be a step towards the spark and arc spectrum; but I was not able to make the change. Until the contrary is proved, I must consider the flame and electric spectra of strontium to be different.

I was unable to obtain chloride of strontium which showed no trace of the sodium line when introduced into a spark; but the hydroxide made by its dissociation, when put, as soon as it was made, into an electric spark or arc, showed a spectrum in which the sodium line was no stronger than it was in a spark or arc passing in the air.

When revising my spectroscopic research on chloride and hydroxide of strontium, in collaboration with M. Depaire, we undoubtedly found that, on analysing the rays from the inner cone of an oxy-coal-gas blowpipe saturated with chloride or hydroxide of strontium, we could see neither the second nor the third violet-blue line discovered by Bunsen in the electric spectrum, and this when using a spectroscopic which showed both these lines in a spark or arc saturated with chloride of strontium.

We ascertained definitely that the electric spectrum of strontium was unchangeable, by submitting the chloride and hydroxide of this metal to the same currents that we used for studying the arc spectrum of lithium and calcium, and using the same spectroscopes. In other words, we used a current made by the battery of thirty-three Julien accumulator cells, and a current from the Gramme and Siemens dynamos coupled, attaching carbon electrodes to the Gerard regulator.

We thus found that spectrum analysis of the strong light produced by the contact of the electrodes showed a spectrum, consisting of a continuous spectrum, on which was superposed that of strontium, and that analysis of the arc showed a continuous spectrum, on which was superposed both the strontium spectrum and the lines of the electric spectrum of carbon.

In both cases, the spectrum of strontium was the same as that illustrated by Bunsen in his work on the electric spectrum of chloride of strontium.

The diffused lines seen in the spark spectrum, with or without a condenser, remain diffused in an arc, however

powerful, though to a less degree. At the instant the chloride of strontium is introduced into the arc, the sodium line becomes visible. This line rapidly decreases in intensity, and, long before the bulk of the chloride is volatilised, the sodium line is no stronger than it is in an arc passing in air between electrodes free from strontium. It may therefore be said that there is no connection between the sodium spectrum and the electric spectrum of strontium.

It follows from the above that the flame and electric spectra of strontium have no connection with the luminous spectra of potassium, lithium, and calcium, and that the electric spectrum of strontium is unchangeable in the conditions under which my researches were carried on.

(To be continued).

THE EAST LONDON TRADES INDUSTRIES AND ARTS EXHIBITION, AND GENERAL EXHIBITION OF THE WORK OF STUDENTS IN POLYTECHNICS AND TECHNICAL INSTITUTES.

WE have great pleasure in referring to this Exhibition, which is to take place in June. Every movement which can induce the people of the East End to seek elevation as individuals and a class, by the advance of the arts and industries in which they are engaged, deserves the warmest support. Our progress as a nation would, however, be much brightened if we could be induced to abandon our delusive system of examinationism. We have just seen its failure on a magnificent scale in the recent collapse of China, the country where competitive examination was first devised, and, after being carried out for centuries, has proved ruinous alike morally and intellectually. Shall we take this lesson to heart?

The departments of the forthcoming Exhibition are announced as a special section for the work of individual craftsmen; secondly, a section for the work of apprentices and of students at the London Polytechnics; and thirdly, a women's section. Unfortunately these sections have relatively little connection with the industries and arts in which we feel the greatest interest.

The technical training of students is of the greater importance, since it is not so much the rank and file of our industrial army, as its leaders,—managers, overlookers, foremen, and even the heads of establishments,—who are not fully on a par with their rivals in Germany, Switzerland, and Belgium.

We are doubtful as to the policy of introducing concerts and other entertainments in connection with an industrial exhibition. Amusements seem to be coming too much to the front, not merely at the People's Palace, but at the Imperial Institute and at certain so-called Aquariums.

We hope that ample funds may be secured for the projected Exhibition, and that they may be expended in promoting the technical prosperity of East London—hence of the Empire at large.

Molybdic Acid as a Reagent for Alcohol.—E. Merck.—The author finds, on experiment, that even minimum traces of alcohol can be detected in aqueous solutions by his special molybdic acid (Acidum molybdenic, pur.). The sensitiveness of this test extends for ethylic alcohol to 0.02 per cent, and for methyl alcohol to 0.2 per cent. Molybdic acid is dissolved in concentrated sulphuric acid, and the solution thus obtained is stratified in a test-glass at about 60° below the liquid under examination. At the surface of contact of the two liquids there appears a distinct blue ring, the more intense in colour the larger the proportion of alcohol. On shaking the blue zone disappears, but reappears on the addition of more molybdic acid. The reaction is not specific for alcohol.—*Chemiker Zeitung*.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 5th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 140).

*32. "Note on the Use of Certain Phosphorescent Substances in rendering X Rays Visible." By HERBERT JACKSON.

In a former paper, on "Observations on the Nature of Phosphorescence" (*Trans.*, 1894, 734), the author drew attention to the similar nature of the phenomena of phosphorescence obtained with various substances placed either inside or outside of a vacuum tube.

Since the publication of that paper the work has been continued, mainly with a view to studying the relation of phosphorescence to the chemical structure, and more especially to the spectra of the substances which exhibit the phenomena. The present note is put forward because the author's experience has enabled him to obtain useful results in the attempt to render certain structures, &c., visible by means of the radiations, the effect of which on photographic plates has latterly attracted so much attention.

The existence of something proceeding from a vacuum tube capable of penetrating many otherwise opaque bodies was first made public by Lenard. The author employed at the time, and has since used, such substances as ebonite, metals, and other opaque sheets, as windows or covers to vacuum tubes in studying phosphorescence with such receptive substances as the platinicyanides, the oxides and carbonates of many metals, and the sodium, potassium, and lithium haloids.

The knowledge of the nature of the radiations which induce phosphorescence in many substances outside a vacuum tube has recently been very greatly added to by Professor Röntgen's discovery that they exhibit none of the phenomena of refraction, diffraction, and interference. To this important discovery he has added the interesting observation of the relative transparencies of bone and flesh.

The vacuum tube most suitable for showing the phenomena, in the writer's experience, is a slight modification only of one invented by Mr. Crookes to illustrate the heating effect of focussed radiant matter.

It consists of a concave aluminium cathode and a platinum anode. The latter is inclined at an angle of 45° , and spreads the rays from the cathode in every possible direction, apparently by scattered reflection.

Such a tube has been regularly employed by the author in experiments upon the phosphorescence of the platinicyanides, and of some three hundred other substances, and was first used by him in January, 1894. About seventy tubes were made in the attempt to obtain the best results, but so far the one described has proved to be the most active.

To obtain good results the vacuum must be high. Apparently the nature of the residual gas does not affect the working of the tube in any marked manner. Both Dr. Norman Collie and the author have tried a number of gases without noticing any marked difference. This may be largely due to the fact that if a mercury pump be used a very considerable percentage of the residual gas is the vapour of that metal.

The most brilliantly phosphorescent substance yet obtained is potassium platinicyanide. This salt crystallises with three molecular proportions of water, and is most active in its fully hydrated state. It effloresces, and should therefore be used in such a way that either it cannot lose water or can be readily moistened. If this platinicyanide be painted on to black cardboard, or thin

vulcanite, &c., its phosphorescence will enable transparent and opaque objects to be clearly differentiated.

The particular potassium salt was chosen from considerations of the brilliant expanse of blue seen in the spectrum of compounds of that metal. Many of the other platinicyanides have been tried, as well as a number of the platamine salts. With none of them is the amount of light equal to that of the potassium salt.

A study of the phenomena during the exhaustion of the tube shows that the rays (it is convenient to speak of rays) proceeding from the concave cathode meet apparently at the centre of curvature and diverge in a solid cone. As the vacuum becomes higher this cone narrows until, when the exhaustion required for the maximum phosphorescence outside the tube is attained, it apparently becomes a straight line.

If, as at present observation seems to indicate, the rays from the cathode are still brought to a focus at the centre of curvature, the fact that they proceed thence in a straight line gives a material aspect to the phenomenon, as this would be the behaviour of particles coming at right angles from the surface of a concave disc, and colliding at the centre of curvature. This, however, would require the assumption that the particles are non-elastic. It is possible that only the centre of the electrode is implicated at high exhaustions. The author is conducting experiments with a view to settle this question of the path of the rays. It does not seem probable that the radiation is confined to the centre, because a straight cathode gives none of the effects observed when the concave form is used. When the rays meet the reflecting platinum plate, which is conveniently, but not necessarily, made the anode, they are scattered by the relatively coarse surface of the metal, a very small circle upon which becomes the radiant. This is shown by experiments with phosphorescent substances placed upon the platinum, and by examining the tube through a pin-hole in an opaque metal sheet by means of a phosphorescent screen. The results obtained are only consistent with the source of illumination being a point or a very small circle. The alternative to the view that the cathode is the true original source of the exciting cause, and that the rays proceed from the glass, is disproved by using flat and curved tubes. A point as the illuminative source would be obtained if rays proceeded at right angles from the surface of a curved glass, but not from a flat one.

In his previous paper the author attempted to show that all the phenomena of phosphorescence, either inside or outside a vacuum tube, were best explained on the assumption that the exciting cause proceeding from the cathode was of the nature of light, or was capable of setting into vibration the residual gas particles so as to give rise to undulations of the nature of light. Professor Röntgen has expressed an opinion in favour of longitudinal vibrations. The author adheres at present to the notion of transverse vibrations, and hopes before long to bring further experimental evidence before the Society in dealing with his work on the relation of the spectra of substances to their phosphorescence.

DISCUSSION.

Sir JOSEPH LISTER remarked on the probable importance to medicine and surgery of the discovery that the shadows produced by the Röntgen rays could be rendered visible to the naked eye in the manner which had been demonstrated by Mr. Jackson.

Dr. ARMSTRONG thought it would be found, when Mr. Jackson's full communication was studied, that he had not only materially advanced the application of Röntgen's most remarkable discovery, but also added much to our knowledge of the phenomena concerned. His success was due to no chance observations, but was the outcome of prolonged, thoroughly scientific study of phosphorescent phenomena, and a development of his previous work.

It was certainly very startling to see, with the aid of a

mere screen held before the eyes, the bones in the foot right through the boot, and to learn that a photograph could be secured in the merest fraction of a second with the aid of such a screen. He believed that Mr. Jackson was of opinion that there were a great variety of Röntgen radiations, and that different objects were opaque to these in different degrees; so that it might ere long be possible, by properly selecting the radiations, to distinguish objects much more closely related than bones and flesh.

*33. "The Union of Carbon and Hydrogen." By WILLIAM A. BONE, M.Sc., Ph.D., and DAVID S. JORDAN, M.A., B.Sc.

Two years ago one of the authors, in conjunction with J. C. Cain (*Proc. Chem. Soc.*, 1894, 56), observed that when a mixture of cyanogen and hydrogen is fired in a long lead coil with a volume of oxygen insufficient to burn all the carbon present to carbon monoxide, a small amount of methane, varying from 1.0 to 1.7 per cent, according to the composition of the original mixture, was found among the products of explosion. This seemed to indicate the possibility of the formation of methane by the union of its elements at the high temperature of the explosion wave, and the authors undertook the following experiments, with a view of testing this hypothesis. They have investigated (1) the effect of heating carefully purified carbon (obtained by heating sugar charcoal in chlorine and subsequently in hydrogen until all the chlorine was expelled) in a glazed Berlin porcelain tube to white heat, in an atmosphere of dry hydrogen free from hydrocarbons; and (2) the action of carbon upon hydrogen at the temperature of the electric arc.

In the first series of experiments the porcelain tube was heated in a Fletcher injector furnace by means of an air-coal-gas blowpipe. In order to avoid the possibility of the diffusion of furnace gases through the porcelain tube, it was placed inside a wider tube of the same material, and a current of hydrogen was passed through the annular space between them. Several blank experiments were performed, in which hydrogen free from hydrocarbons was passed through the inner tube and through the jacket, whilst the tubes were maintained at a white heat; samples of hydrogen taken from the inner tube during the course of an experiment were found, on analysis, to contain no carbon compound. The purified carbon, after being dried over phosphoric anhydride for two months, was strongly heated in a hard glass tube attached to a Sprengel air-pump, and was then sealed up in a vacuum with quick-lime. This carbon was introduced into the inner porcelain tube, and was heated to white heat in a current of hydrogen free from hydrocarbons, whilst simultaneously a current of the same hydrogen was passed through the space between the inner and outer tubes. Samples of the exit gases from the inner tube were afterwards carefully analysed; they were found to contain no acetylene or other unsaturated hydrocarbon, but about 1 per cent of methane. In another experiment, a volume

of hydrogen was enclosed in the inner tube, heated for three hours in contact with the carbon; on subsequently analysing the gas, it was found to contain nearly 2 per cent of methane.

In the second series of experiments, the electric arc was formed between terminals of purified gas-carbon in an atmosphere of dry hydrogen free from hydrocarbons, contained in a glass globe standing in a trough over mercury. Each of the carbon terminals, which had been previously strongly heated for several hours in a hard glass tube connected with a Sprengel air-pump, was attached to a stout copper wire, which in turn was fixed into a piece of narrow glass tubing bent into U shape and filled with mercury. The limb of the U-tube bearing the carbon was then thrust into the globe from below the surface of the mercury in the trough. The top of the globe was drawn out and sealed to a three-way tap, by means of which connections could be made, on the one hand, with an air-pump for the supply of hydrogen, and, on the other hand, to a nitrometer full of mercury, which served to collect samples of the gas in the globe at intervals during an experiment.

At the outset of an experiment, the globe was exhausted of air by attaching it to a working air-pump until it was completely filled with mercury. Then dry hydrogen was introduced, and the arc passed between the terminals for about a quarter of an hour. The globe was again exhausted, and finally filled with the dry purified hydrogen. The arc was then passed for a period of time varying from thirty minutes in the first experiment to two hours in the last, and at the end of five, fifteen, thirty, &c., minutes in each experiment, samples of the gas were drawn off for analysis.

Composition of the Gases.—The gases were always found to contain small amounts of hydrocyanic acid, due no doubt to the presence of a little nitrogen in the hydrogen employed. Acetylene was also present in considerable quantity, and was detected by passing the gas through an ammoniacal solution of silver chloride, when a copious precipitate of silver acetylide was formed. A detailed analysis of the gases showed, however, that, in addition to acetylene or other unsaturated hydrocarbon, they invariably contained an appreciable amount of some saturated hydrocarbon, most probably methane.

The gases were analysed in a modified form of the McLeod apparatus. A large volume of the gas was successively treated with solid potash, fuming sulphuric acid, acid solution of cuprous chloride, and a dilute solution of potash, in order that all hydrocyanic acid, unsaturated hydrocarbon, and any traces of carbonic oxide might be removed; a portion of the residual gas was then exploded with excess of air, free from carbon dioxide, and the contraction and absorption by potash solution after the explosion determined. Finally, the excess of oxygen was absorbed by means of alkaline pyrogallate, and the residual nitrogen measured.

The results of the analyses are tabulated in percentages.

Experiment.	Gases drawn off after	Minutes.						
		5.	15.	30.	45.	60.	90.	120.
A ..	Absorption by solid potash [hydrocyanic acid] ..	0.20	1.01	1.51	—	—	—	—
	Absorption by fuming sulphuric acid and cuprous chloride solution, i.e., ethylene, acetylene ..	5.10	8.43	9.85	—	—	—	—
	Methane	1.32	2.20	2.46	—	—	—	—
B ..	Absorption by solid potash [hydrocyanic acid] ..	0.11	0.20	0.12	0.20	—	—	—
	Absorption by fuming sulphuric acid and cuprous chloride solution, i.e., ethylene, acetylene ..	2.13	4.99	6.41	8.08	—	—	—
	Methane	0.64	1.38	2.26	2.26	—	—	—
C ..	Absorption by solid potash [hydrocyanic acid] ..	trace	trace	0.10	—	0.53	1.00	0.39
	Absorption by fuming sulphuric acid and cuprous chloride, i.e., ethylene, acetylene	2.12	4.70	6.16	—	6.83	6.42	7.59
	Methane	1.00	1.63	2.37	—	2.71	2.15	2.62

In all three experiments an alternating current from a dynamo was used. In Experiment A, the voltage was 160, and in B and C between 40 and 60, but it was extremely difficult to maintain a constant voltage throughout a long experiment.

34. "Note on the *αα*-Dimethylglutaric Acids." By WILLIAM A. BONE, M.Sc., Ph.D., and W. H. PERKIN, Jun., F.R.S.

The authors are now able to confirm the observation of Thorpe and Auwers (*Ber.*, xxviii., 623) that the acid melting at 105–107° which they described in a paper published last year (*Trans.*, 1895, 416), is really an equimolecular mixture of trans- and cis-dimethylglutaric acids melting at 140–141° and 127° respectively. This equimolecular mixture, which in many respects behaves like a homogeneous substance, having, for example, a fairly sharp and constant melting-point, may be resolved into its constituent acids by careful treatment with acetyl chloride, when the cis-acid yields an anhydride, whilst the trans-acid is unchanged, or by fractional precipitation of the acid calcium salts, that of the trans-acid being least soluble.

35. "The Symmetrical Dimethylsuccinic Acids." By WILLIAM A. BONE, M.Sc., Ph.D., and W. H. PERKIN, Jun., F.R.S.

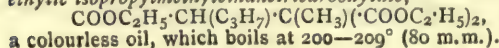
During the course of their investigations on trimethylsuccinic and *αα*-dimethylglutaric acids last year, the authors obtained a considerable quantity of ethylic dimethylcyanosuccinate as a by-product of the action of potassium cyanide on ethylic *α*-bromopropionate in alcoholic solution (*Trans.*, 1895, 416). On hydrolysing this ethereal salt by means of concentrated hydrochloric acid they obtained a mixture of trans- and cis-dimethylsuccinic acids, which they were able to separate either by fractional crystallisation from water or by a fractional precipitation of their calcium salts. After studying the literature of the subject, the authors found that the properties of the dimethylsuccinic acids which they had obtained differed considerably from those assigned to them by previous investigators, and they therefore submitted these acids and their anhydrides to a careful examination.

They also prepared the dimethylsuccinic acids by the action of ethylic *α*-bromopropionate on the sodium compound of ethylic methylmalonate, subsequent hydrolysis of the resulting ethereal salt by means of alcoholic potash, and then heating the tribasic acid so obtained to 200° until all evolution of carbonic anhydride had ceased. The resulting acids were in all respects identical with those obtained by the first method.

Trans-dimethylsuccinic acid when pure melts at 209°, and is very much less soluble in water than the cis-acid, which melts at 129°. The calcium salt of the trans-acid is, however, much more soluble in water than that of the cis-acid. Each acid, when treated with acetyl chloride or acetic anhydride, yields its own anhydride, a fact first observed by Otto and Rössing (*Ber.*, xx., 2736) and confirmed by Bischoff; the trans-anhydride melts at 43° (not 38° as given by Bischoff) and is less stable than the cis-anhydride, which melts at 88°, and is completely transformed into the last-named substance on prolonged heating with acetic anhydride. Both acids, on distillation at atmospheric pressure, yield the cis-anhydride. Each anhydride dissolves in hot water, yielding its own acid, not, as some authorities have stated, a mixture of the cis- and trans-acids.

36. "The Cis- and Trans-methylisopropylsuccinic Acids." By WILLIAM HENRY BENTLEY, WILLIAM HENRY PERKIN, Jun., and JOCELYN F. THORPE.

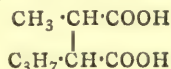
The authors have studied the action of ethylic *α*-bromoisovalerate on the sodium compound of ethylic methylmalonate in alcoholic and in xylene solution, and find that in both cases the product of the reaction consists of ethylic isopropylmethylmethanetricarboxylate,—



a colourless oil, which boils at 200–209° (80 m.m.).

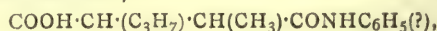
This oil, on hydrolysis and subsequent elimination of carbon dioxide, yields a mixture of cis- and trans-methylisopropylsuccinic acids, which are separated by methods described in detail in the paper.

Cis-methylisopropylsuccinic acid,—

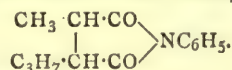


melts at 125–126°, and, when heated with hydrochloric acid at 180°, is partially converted into the trans-modification; when distilled or digested with acetic anhydride, it yields a liquid anhydride boiling at 138–140° (35 m.m.).

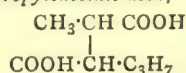
The *anilic acid*,—



melts at 153°, and, at a somewhat higher temperature, loses water with formation of the corresponding *anil*,—



Trans-methylisopropylsuccinic acid,—



melts at 174–175°, and is much less soluble in water than the cis-acid; when distilled under diminished pressure, or when digested with acetic anhydride, it is converted into a solid anhydride melting at 46°; and this, when repeatedly distilled at ordinary pressures, is converted into the anhydride of the cis-acid.

The *anilic acid* obtained from trans-anhydride by treatment with aniline melts at 160°, and a few degrees above this temperature loses water and is converted into the *anil* of the cis-acid.

The authors have also prepared the methylisopropylsuccinic acids from ethylic isopropylethanetricarboxylate, which Roser (*Annalen*, ccxx., 272) first synthesised by the action of ethylic *α*-bromoisovalerate on the sodium derivative of ethylic malonate. When this ethereal salt is acted on with sodium ethoxide and methylic iodide, ethylic methylisopropylethanetricarboxylate is produced, and from this ethereal salt the methylisopropylsuccinic acids may be obtained by the method described above.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxlii., No. 9, March 2, 1896.

Observations on Photography through Opaque Substances.—A. d'Arsonval.—Already inserted.

On Invisible Radiations Emitted by Phosphorescent Bodies.—Henri Becquerel.—Will be inserted in full.

Reply to the Observations of H. Poincaré on the Theory of Kathodic Rays.—G. Jaumann.—A purely mathematical paper, not suitable for abstraction.

Observations on the Foregoing Memoir.—H. Poincaré.—The author explains his use of the term "ray."

Exhibition of Proofs obtained by Röntgen's Method.

Dark Light: a Reply to certain Criticisms.—Gustave Le Bon.—Already inserted.

Diffusion of the Röntgen Rays.—A. Imbert and H. Bertin-Sans.—This paper will be inserted in full.

The Photographic Representation of the Relief of a Medal obtained by means of the Röntgen Rays.—J. Carpentier.—Will be inserted in an early number.

Passage of Röntgen's Rays through Liquids.—MM. Bleunard and Labesse.—Already inserted.

Discovery and Extraction by means of a Röntgen Photograph of a Needle embedded in the Human Hand.—Pierre Dalbet.—An instance of the successful application of Röntgen's rays in surgery.

Applications of Röntgen's Method.—Ch. Girard and F. Bordas.—Five detections of enclosed objects.

Extraction of Rhodinol from the Essence of Pelargonium and from the Essence of Roses.—Ph. Barbier and L. Bouveault.—The authors have established the identity of these two essences by a study of their chemical properties and the identification of their derivatives. The proportion of rhodinol is small in each case, not exceeding 20 per cent.

Preparation of Silicichloroform, Silicibromoform, and some Derivatives of Triphenyl-silicoprotane.—Charles Combes.—The author will show in a future paper how he has effected his purpose by employing a tertiary amine.

Oxidation of Crotonic Aldehyd.—E. Charon.—Not suitable for abstraction.

Journal für Praktische Chemie,
New Series, Vol. li., Part 12.

On Phenomena of Isomerisation in the Series of the Carbonyl Compounds of Chlorised Alcohols and Haloid-substituted Oxides of the Ethylenhydrocarbons.—Al. Faworsky.—In this voluminous memoir the author expounds the action of hypochlorous acid upon bi-substituted acetylenhydrocarbons.

Syntheses of Quinazolin Compounds.—St. von Niementowski.—The author describes the synthesis of δ -oxyquinazolin, of δ -oxymeta-toluquinazolin, of β -methyl- δ -oxyquinazolin, of β -methyl- δ -oxymeta-toluquinazolin, of β -ethyl- δ -oxyquinazolin, of β -ethyl- δ -oxymeta-toluquinazolin, of prognonmeta-toluid, of β -isopropyl- δ -oxyquinazolin, of β -isopropyl- δ -oxymeta-toluquinazolin, and of isobutylra-meta-toluid.

Synthesis of Antipyrin, a Reply to F. Stolz.—R. von Rothenburg.

Cases of Isomerism in the Pyrazol Series, a Reply to L. Kron.—R. von Rothenburg.

On Chemical Equivalence.—R. von Rothenburg.

On the Phthalein-melt.—R. von Rothenburg.

These four strongly controversial papers have already reached the stage which our German colleagues aptly term "unerquicklich," and are passing on into the region of personalities.

Constitution of the Diazo-benzene Compounds.—R. Walther.—A criticism of the results of Meldola and Streatfield.

On the Most Recent Views of Herr Hantzsch on the Diazo-compounds.—Eug. Bamberger.—A criticism of the views of Hantzsch on the constitution of the diazo-compounds.

The Production of Pinakones by the Reduction of Aromatic Ketones.—K. Cebo and K. Schmitz.—The regularity established by the experiments of the authors affords the means of demonstrating, by a simple reduction with zinc-powder and glacial acetic acid, whether a ketone contains its carboxyl group in direct combination with an aromatic group or not.

Parts 13 and 14.

Researches from the Laboratory of the University of Freiburg, in Breisgau.—These researches comprise a paper by Ad. Claus and Alex. Seelemann, on the

sulphonic acids of isoquinolin, and a memoir on isoquinolin by Ad. Claus and C. Gutzeit.

Synthetic Researches in the Pyrazol Series. Parts II. and III.—R. von Rothenburg.

Calorimetric Researches.—F. Stohmann and Raym. Schmidt.—This paper discusses the thermic value of the amides and anilides of monobasic acids.

The Solubility in Water of Certain Substitution Derivatives of Benzene.—W. Vaubel.—The author does not accept the rule proposed by Carnelley and A. Thomson, that for one group of isomeric organic compounds the series of solubilities is at the same time the series of the melting-points,—i. e., the most soluble substance is also the most fusible. There occur a number of exceptions, especially among the kresols, nitrophenols, nitro- and oxybenzoic acids, and probably among the toluidines and nitro-anilines.

Remark on the Memoir of Fileti and Ponzio on the Transformation of the Ketones into α -Diketones.—L. Claisen.—The author accepts the accuracy of the conclusion of Fileti and Ponzio, but protests against their having regarded his former opinion as ultimate.

Reply to the Memoir of R. von Rothenburg on the Constitution of the n -Phenyl-pyrazolones.—L. Claisen.—The author considers any further discussion with C. von Rothenburg as useless.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxiii., No. 1.

This issue contains no chemical matter.

MEETINGS FOR THE WEEK.

TUESDAY, 31st.—Institute of Civil Engineers, 8.

WEDNESDAY, April 1st.—Society of Public Analysts, 8. "The Bacteriological Examination of Water for the Typhoid Bacillus," by T. H. Pearmain and C. G. Moor, M.A. "Note on the Estimation of Formic Aldehyd," by Harry M. Smith. "The Composition of Human Fat," by C. A. Mitchell, B.A.

FRIDAY, 3rd.—Quekett Club, 8.

THE MANUFACTURE OF EXPLOSIVES.

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THE CHEMICAL NEWS.

Vol. LXXIII., No. 1897.

THE PHOTOGRAPHIC REPRESENTATION IN RELIEF OF A MODEL OBTAINED BY MEANS OF THE RÖNTGEN RAYS.

By J. CARPENTIER.

IN the course of researches which I have undertaken, to combine some numerical data on the permeability of metals by the Röntgen rays, I have been led to make an experiment having as its object the photographic representation of a model in relief.

The model upon which I have operated is a bronze coin. To obtain an image of the subject which it bears, the figure, and the inscription, I placed upon this medal a slender circle of aluminium well-reheated. By the stroke of a fly-wheel I have obtained a hollow mould in aluminium of the relief of the coin. This slender mould, deposited on a frame formed of several layers of black paper, and containing a photographic plate, was submitted to the action of a Crookes phial.

On account of the fact that the hollows present a less resistance to the passage of the rays than do the projections, the corresponding parts of the proof are the blackest; the image has the appearance of a negative. Small proofs on paper, obtained by contact, have the appearance of a positive. Enlargements obtained on setting out from a positive on glass are in all respects like the proof itself.

The distinctness of these various images is very great, on account of the precaution taken to interpose between the phial and the plate an opaque screen of brass having a perforation of 1 c.m. in diameter.

The relief of the bronze coin, although concentrated in appearance, measures only $\frac{8}{1000}$ m.m. The round disc of aluminium in the parts not stamped is of $\frac{1}{2}$ m.m. in thickness.

The phial has been but little charged, and the exposure was only four hours. In order to define the intensity of the active radiation, I compared its effect on the parts of the plate not protected by the mould with the effect produced on a similar photographic plate by an ordinary candle placed at a distance of 1 metre. I found that the action of the phial, under the conditions indicated, was equal to the action of the candle for two seconds. It would be useful for comparison if experimentalists would take care to indicate the strength of the field in which they operate. It is evident that other bodies, even though non-metallic, would be suitable for the same experiment. —*Comptes Rendus*, cxvii., p. 526.

PHOTOGRAPHIC RESEARCHES ON THE RÖNTGEN RAYS.

By AUGUSTE and LOUIS LUMIÈRE.

IF the photographic method has just attained a new success with Prof. Röntgen's experiments, it is to be expected that it will still render greater services for the study of the X rays when the photographic preparations shall be better adapted to the properties of these rays. We are now engaged with the study of their action upon sensitive substances.

We remarked at first that the Röntgen rays act in the same manner upon gelatino-bromide plates coloured and rendered sensitive to the various spectral regions. Thus plates sensitised for red, for yellow, or for green, give

exactly the same impression, all other things being equal, on condition that they have the same general sensitiveness for white light.

If we have photographic plates of different sensitiveness for white light, it seemed to us interesting to examine if the proportion of sensitiveness is the same for the X rays. We have operated upon preparations in which the times necessary to obtain the same impression with a constant source of luminous radiation are respectively as 1.8 and 30, and we have observed that, within the range of our experiments, these proportions are exactly preserved for Röntgen's rays.

Another series of experiments had the object of studying the absorption of these rays by sensitive strata, and of comparing it with that of luminous rays in analogous conditions. To this end we exposed, under a screen formed of letters cut out of a thin sheet of copper, a packet of 250 leaves of silver gelatino-bromide, superposed and sheltered by known methods from the luminous rays. We allow the X rays to act for ten minutes, when we find, on developing, that the 150th leaf still presents an impression.

In order to judge of the importance of the absorption due to the passage of the rays through the paper serving as a support for the silver gelatino-bromide, we compared the images obtained on substituting, in the foregoing experiments, paper not sensitised for the gelatino-bromide paper. After a series of trials, we found that about 300 leaves of white paper were required to produce the same absorption as 150 leaves of sensitive paper. The layer of gelatino-bromide employed absorbs, therefore, the X rays in the same manner as the paper which serves as its support. The absorption of the X rays by sensitive paper is therefore exceedingly feeble. This property may even serve as a characteristic of these rays. If, in fact, we seek to reproduce the same series of experiments with different sources of light,—sun-light, the electric light, the Auer burner, &c.,—we find that, after passage through a very small number of sensitive leaves, the light has no action upon the subjacent papers.

The first proof having been attained with sun-light, with an impression comparable to the first leaf of the former experiment, we find that the sixth leaf no longer presents a trace of an image.

This extraordinary penetration of the X rays, and their very slight absorption by sensitive preparations, seems to afford a method of searching for these rays in sources of light of greater or less intensity. Except Crookes tubes, and similar tubes, the photographic effects which we have observed with the electric arc, the Auer burner, the petroleum lamp, &c., are due only to the penetration of the luminous rays properly so called, or to heating thermic rays, which are very rapidly extinguished by the folds of paper.

We have never been able to find the presence of X rays in these sources of light.—*Comptes Rendus*, cxvii., p. 382.

DIFFUSION OF THE RÖNTGEN RAYS.

By A. IMBERT and H. BERTIN-SANS.

IN the course of experiments undertaken in order to increase the intensity of the sheaf of Röntgen rays utilised in photography, we have observed very definite phenomena of diffusion, the existence of which seems able to contribute to a determination of the nature of the new rays.

In order to observe the existence of the diffusion we have received the rays emanating from a Crookes tube upon plane plates of different bodies, and we have arranged at the side of the tube a sensitive plate, covered with a double coat of needle-paper, in a direction nearly normal to that which the mean region of the sheaf would have if it reflected regularly. A thick plate of copper was interposed between the Crookes tube and the photographic

plate, in order to screen the latter from any direct radiation.

To prove the existence of the Röntgen rays sent back by the reflecting or diffusing plate, we fixed upon the photographic plate a crystal of quartz (opaque to these rays) fixed in a setting of cork (transparent to the same rays); a member of a metallic class (and consequently opaque) was, besides, each time interposed between the paper covering the sensitive plate and the surface of the setting of cork in contact with the paper.

Many comparative experiments have, further, been made on the same plate, protecting successively the different parts of the latter by means of thick metallic plates absolutely opaque.

We have used at first, as a reflecting or diffusive body, one of the metal plates of an Epstein condenser, and we have found that, after an exposure of ten minutes, the photographic plate was distinctly acted upon by the Röntgen rays, whether the plate insulated by its glass foot was or was not covered with varnish, or was connected with earth or with one or the other pole of a Wimshurst machine giving sparks of 10 c.m. In each of these cases the plate has been acted on with an equal intensity, the quartz has always remained opaque, the cork always transparent, and the number of the metallic series has always been reproduced through the cork. Further, in the comparative experiment made with a fourth of each plate, causing the Crookes tube to act but suppressing the metallic plate, we have never obtained any impression or proof that our plates were entirely protected against direct radiation.

Identical results were obtained on substituting a plate of paraffin for the metal plate.

On the contrary, a plate of cork of 7 m.m. in thickness, very transparent to the Röntgen rays, gave only a scarcely perceptible impression of the number of the metallic series. It was the same with plates of glass, although this substance is relatively very opaque to the Röntgen rays; the quantity of diffused rays has also been scarcely more considerable with ground glass.

In another set of experiments we caused the Röntgen rays to traverse a glass tube of 0.12 metre in length, closed with two stoppers of cork covered with paraffin, in which a vacuum could be produced. The intensity of the photograph of a fine metallic grating was scarcely greater when we made in the tube a vacuum of 6 m.m. of mercury.

On attempting to cause a slender sheaf of rays approximately parallel, obtained by the aid of two circular diaphragms of the same diameter to be reflected from a polished metal plate, the sensitive plate, after exposure for half an hour, presented no visible trace of impression.

Hence there is room to infer that if the Röntgen rays are reflected regularly under the conditions of our experiments, this takes place only to a very slight degree. On the contrary, they may be diffused in a very great quantity, and the diffusion appears to depend more on the nature of the substance than on the degree of polish of the diffusing substance. This fact would lead us to ascribe to the new rays a very small wave-length, such that it is not possible to realise the degree of polish necessary for determining their regular reflection.

The proofs obtained have further shown us, as regards cork and quartz, the different degrees of transparency of the different bodies employed for diffused rays. We reserve it to ourselves to check this last result, and we have commenced for this purpose a series of experiments by which we hope, either by diffusion or transmission, to obtain information on the homogeneity and the complexity of the sheaf of the new rays.—*Comptes Rendus*, cxxii., No. 9.

New Series of Sulphophosphides: the Thiophosphites.—M. Ferrand.—The author has obtained and examined the cuprous, ferric, silver, nickel, chromium, cadmium, mercury, and aluminium salts.—*C.R.*, cxxii., No. 10.

THE COMPOSITION OF WATER. A SHORT BIBLIOGRAPHY.

By T. C. WARRINGTON, B.A.

(Continued from p. 146).

III. Gravimetric Methods.

A. The Combination of Weighed Quantities of Hydrogen and Oxygen to form Water (Weighed in some cases).

(29). 1889. Lord RAYLEIGH.

"On the Composition of Water." (Read March, 1889).

Proc. R. S., (1888-9), xlv., p. 425.

Chem. News, (1889), lix., p. 147.

Abs. J. C. S., (1890), lviii., p. 330.

Beibl. Wied. Ann., (1890), xiv., p. 2.

The gases were weighed in globes, from which they were pumped into a eudiometer and there burnt.

(30). 1891. E. H. KEISER.

"On the Atomic Weight of Oxygen." (March, 1891).

Amer. Chem. J. (1891), xiii., p. 253.

Chem. News, (1891), lxiii., p. 197. (Reprint).

Abs. J. C. S., (1891), lx., p. 1154.

Beibl. Wied. Ann., (1891), xv., p. 679.

The author, after criticising the work of Noyes (45) and defending himself goes on to make a complete synthesis of water by leading oxygen into a vessel containing a weighed amount of hydrogen condensed in palladium.

(31). 1891. E. W. MORLEY.

"Synthesis of Weighed Quantities of Water from Weighed Quantities of Oxygen and Hydrogen Gas."

Proc. Amer. Ass., (1891), xi., p. 185.

(32). 1895. E. W. MORLEY.

"On the Atomic Weight of Oxygen. Synthesis of Weighed Quantities of Water from Weighed Quantities of Hydrogen and Oxygen."

Amer. Chem. J., (1895), xvii., p. 267.

A new method is described. Hydrogen from palladium and oxygen from a globe are burnt together in a special apparatus. Residual water and residual gas are separately measured, giving the ratio of oxygen and hydrogen forming water. A second ratio is obtained from the weight of water and weight of hydrogen, and a third from densities of hydrogen and oxygen and determination of their combining ratio by a method similar to that of Leduc. The full paper will appear in the "Smithsonian Collections."

B. Combination of a Weighed Quantity of Oxygen with Hydrogen to form a Weighed Quantity of Water.

(33). 1820. BERZELIUS and DULONG.

"Nouvelles Déterminations des Proportions de l'Eau, et de la Densité de quelques Fluides Elastiques."

Ann. Chim. et Phys., (1820), xv., p. 386.

Schweigger Journ., (1820), xxix., p. 83.

Thomson's Ann. Phil., (1821), ii., p. 48.

Tulloch, Phil. Mag., (1821), p. 203.

The method followed is that more generally known by the name of Dumas.

(34). 1842. DUMAS.

"Recherches sur la Composition de l'Eau."

Ann. Chim. et Phys., (1843), [3], viii., p. 189.

Compt. Rend., (1842), xiv., p. 537.

Journ. Prakt. Chem., (1842), xxvi., p. 449. (Trans.).

Pogg. Ann., (1842), lvii., p. 150.

(35). 1842. ERDMANN and MARCHAND.

"Ueber die Atomgewichte des Wasserstoffes und des Calciums."

Journ. Prakt. Chem., (1842), xxvi., p. 461.

The method followed is that of Berzelius.

(36). 1842. Dr. CLARK.

"On the Revision and more Exact Determination of Atomic Weights. (Extract from a Letter).

Proc. Chem. Soc., (1842), i., p. 15.

Phil. Mag., (1842), [3], xx., p. 341.

A correction is applied to Berzelius's results to reduce weighings in air to weighings *in vacuo*.

(37). 1884. T. HILDITCH.

"On the Determination of the Atomic Weight of Oxygen."

Chem. News, (1884), xlix., p. 37.

Beibl. Wied. Ann., (1884), viii., p. 342.

The author points out the errors in Dumas' work due to use of impure hydrogen and to not weighing *in vacuo*.

(38). 1890. W. DITTMAR.

"On the Gravimetric Composition of Water." (Preliminary communication. Read Feb. 3, 1890).

Proc. R. S. E., (1891), xviii., p. 320.

Chem. News, (1890), lxi., p. 75.

Beibl. Wied. Ann., (1890), xiv., p. 435.

The author criticises Dumas' calculation of results. In the reprint in CHEM. NEWS considerable additions are made to the original paper.

(39). 1891. W. DITTMAR and J. B. HENDERSON.

"On the Gravimetric Composition of Water."

Proc. Phil. Soc. Glasgow, (1890-1), p. 1.

Chem. News, (1893), lxvii., pp. 54, 68, 77, 90, 104, 115, 126, 139, 151, 164.

Abs. J. C. S., (1893), lxiv., p. 410.

Beibl. Wied. Ann., (1892), xvi., p. 1.

Dumas' work is critically repeated, and a new synthesis is made by a modification of the method.

(40). 1892. A. LEDUC.

"Sur la Composition de l'Eau et la loi des Volumes de Gay-Lussac. (Note).

Compt. Rend., (1892), cxv., p. 41.

Abs. J. C. S., (1892), lxii., p. 1271.

Beibl. Wied. Ann., (1893), xvii., p. 994.

The method of Dumas is adopted with slight modifications.

(To be continued.)

VOLUMETRIC ANALYSIS OF A MIXTURE OF CHLORIDES, HYPOCHLORIDES, AND CHLORATES.

By AD. CARNOT.

It is known that chlorine acting upon alkaline and alkaline-earth hydrates gives rise to chlorides, and at the same time to chlorates, or to hypochlorates, according as the temperature and the concentration are higher or lower. In average conditions the three kinds of salts are formed simultaneously.

A mixture of the same salts is produced if we submit solutions of sodium chloride to electrolysis, according to the processes recently tried for the manufacture of free chlorine and of caustic soda, or of chlorates or hypochlorites.

In these various cases it is of great industrial importance to determine easily the proportion of each of the salts present.

An analogous question occurs when we require to determine the true composition of a chloride of

lime, as this product always contains a little chlorate, even when the sample has been recently and carefully prepared (Lunge and Schoch), and the proportion of this salt increases progressively with time (Pattinson), especially when the bleaching lime has been manufactured with lime partly carbonated (Fresenius).

For the analysis of such a mixture of salts I believe that I may recommend the subjoined method as at once expeditious and accurate. All the determinations are performed successively upon one and the same specimen of the saline solution.

1. We first determine the hypochlorite by the well-known method with sodium arsenite slightly modified. I have satisfied myself that in the conditions of the experiment this reagent exerts absolutely no reductive action upon the chlorate, the liquid being neutral or alkaline.

2. We then acidify with sulphuric acid and add a measured quantity of ferrous sulphate, the excess being titrated with permanganate. We thus determine the chlorate from the quantity of oxygen which it yields up to the ferrous sulphate.

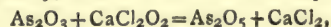
3. Lastly, we determine the total chlorine (derived either from the original chloride or from the reduction of the hypochlorite and the chlorate) by the process with silver nitrate and ammonium sulphocyanide. This process permits us to operate in an acid liquid, like that obtained by the foregoing operation.

Knowing by the two first operations the exact proportions of hypochlorite and of chlorate, we thence deduce the corresponding quantity of chlorine; the last operation then shows, by difference, the quantity of chlorine which existed in the original liquid in the state of chloride. There is no inconvenience here in making use of a determination by difference, since it applies to the salt most abundant and the least important to be exactly determined.

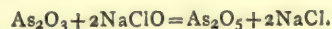
After these general indications, I must give some details concerning the manner of effecting the three successive determinations.

I. The mixture of hypochlorite, chlorate, and chloride taken from the solution of electrolysed sodium chloride, or from the liquid obtained on lixiviating the bleaching lime, is poured into a test-glass. There is then run into it from a graduated burette a standard solution of sodium arsenite, prepared as usual, until the hypochlorite is completely reduced. To find the exact moment when the reduction is completed, we place, with the end of a glass rod, a drop of the liquid upon a porcelain plate in contact with a drop of a solution of potassium iodide and of starch, prepared beforehand by stirring up in cold water 3 grms. starch, raising it to ebullition whilst stirring, adding 1 gm. sodium carbonate, and 1 gm. potassium iodide, and diluting to 500 c.c.

On the mixture of the two drops there appears a blue colour as long as there remains any hypochlorite not reduced. As soon as the mixture ceases to become coloured, we read off the volume of the arsenite liquid, and thus infer the proportion of hypochlorite of hypochlorous acid which has transformed it into arsenic acid; or, consequently, that of the chlorine corresponding.

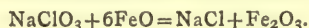


or—



II. We slightly acidify the liquid (which now contains merely chlorate and chloride) with sulphuric acid, and dissolve in it ammonium-ferrous sulphate, in a quantity at least twenty times that of the supposed chlorates. These we heat to about 100°, adding in small successive quantities 5 c.c. of sulphuric acid diluted with 15 c.c. of water. It is best to use a cork-funnel, letting the sulphuric solution fall in drop by drop. After having stoppered the vessel, to avoid contact of air, it is allowed to cool for a short time, and the excess of ferrous salt is then titrated with permanganate. As we know the quantity of ferrous salt which was introduced, we have by dif-

ference the quantity which has been peroxidised at the expense of the chlorate reduced to the state of chloride.



It is thus easy to calculate the proportion of chlorate or of chloric acid, or the corresponding quantity of chlorine.

III. As for the total chlorine, which is now entirely present in the state of chloride, it is determined as follows:—We first remove the rose tint produced by the permanganate by adding a trace of ferrous sulphate, crystallised or in solution. We then add a measured volume of silver nitrate, more than enough to precipitate all the chlorine, and determine the excess of the silver salt by means of ammonium sulphocyanide which has been standardised against silver nitrate. The ferric salt previously formed by the peroxidation of the ferrous salt serves as an indicator, by producing a permanent red colouration as soon as there is no more silver salt to precipitate. As for the arsenic acid produced in the first operation it does not interfere in the least.

In order to avoid the use of too large a quantity of silver nitrate, which would be necessary on account of the large proportion of chlorine to be precipitated, we may make use only of an aliquot part of the solution.

The chlorine found in the state of a chloride in the original liquid is easily calculated by deducting from the total chlorine just determined the two quantities already found in the state of hypochlorite and of chlorate.

The three operations succeed each other without interruption, and without separate preparation, and are completed in a short time. It is useful to check the results by making a second series of determinations to avoid accidental errors.

Numerous experiments have permitted me to find that the method yields results of great accuracy. These experiments have been made with known and very varied quantities of the three salts taken separately, or two by two, or all three taken together. The chlorides and chlorates were weighed in a state of purity; the chloride of lime, which has always a complex composition, was treated with water, and the lixivium was assayed first for hypochlorites, chlorate, and chloride, and it was then assayed anew after the addition of known quantities of alkaline chlorate and chloride.

The discrepancies found between the experimental results and the calculated numbers rarely reached 1 m.grm. when operating upon from 250 to 500 m.grms.—*Comptes Rendus*, cxxii., p. 449.

GAS ANALYTICAL APPARATUS FOR THE EXAMINATION OF AIR CONTAINING FIRE DAMP.

By SIGMUND REICHENBERG,
Royal Hungarian Inspector of Steam-boilers.

THE apparatus is constructed on the principle of Coquilhon's apparatus. Fig. 1 is the elevation. Instead of the bottle, which in ordinary apparatus for gas-analysis contains the closing-liquid, there is employed here a caoutchouc globe, c, which is compressed or allowed to expand by turning the screw, s, to the right or the left, and the mercury which it contains rises into the measuring pipette or flows back. The movement of the screw is taken up by the rod d by means of the tube t. The measuring pipette, m, and the caoutchouc ball, c, are immersed in the glass cylinder, g, which is filled with water. The measuring pipette, m, communicates as usual with the atmosphere (but is capable of being shut off), and with the absorption tube, a. At s₁ and s₂ there are screw-clamps for the caoutchouc tubes serving for communication.

Fig. 2 shows the combustion tube (B, Fig. 1) in actual size; p is the spiral of platinum wire, which can be made

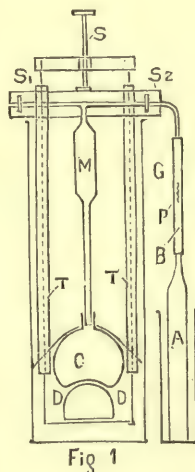


Fig. 1

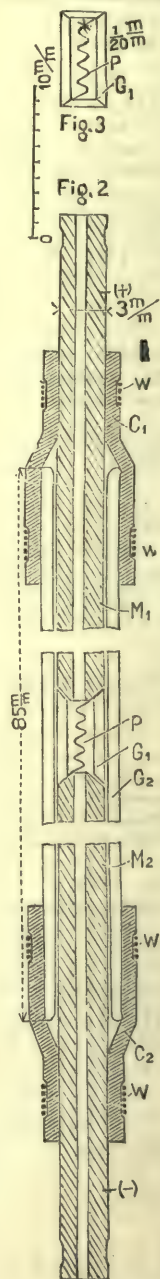


Fig. 3

Fig. 2

red-hot by a galvanic current. The current is conducted by the metal tubes M₁ and M₂. Through these tubes there flows simultaneously the air containing methane out of the measuring pipette M (Fig. 1) into the absorption tube (A, Fig. 1) and back again; whereby the methane is completely burnt by close contact (twice repeated) with the ignited platinum spiral. The conical (or rather, globular) ends of the metal tubes, M₁ and M₂, fit suitably in the ground glass apertures of the small glass tube, G, in which the contact of the metal tube takes place with the platinum spiral. To ensure stability, the ends of the platinum spiral are bent over around the edges of the small glass tube, as shown separately in Fig. 3. The glass tube, G₂, which infolds the metal pipe, is closed by

the caoutchouc tubes C_1 and C_2 . For a more thorough closure, the caoutchouc tubes are connected with thin wire, w. Before applying the fourth wire binding the caoutchouc tube concerned is drawn up and the wire binding is applied while it is in this state of tension. In this manner the elasticity of the caoutchouc tube presses the ends of the metal tubes, M_1 , M_2 , into the mouths of the small glass tube, G, where there arises better contact for the conduct of the galvanic current with the platinum spiral. The conductive wires of the galvanic current are connected with the metal tube at $+a$ -. The absorption tube (Fig. 1, A) contains a weak alkaline solution, to absorb the carbonic acid generated. The absorption tube is, as usual, filled with glass piping.

Before the measurement takes place, the air under examination is passed from the measuring pipette into the absorbent tube, where the air is saturated with moisture. The decrease of volume after the combustion of the methane divided by 3 gives the proportion of methane.

To avoid errors in measurement the internal parts of the apparatus, especially the combustion-tube, should be kept clean.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 149).

CHAPTER IX.

CHEMICAL RESEARCHES ON SULPHATE, SULPHIDE, CHLORIDE, AND CARBONATE OF BARIUM.

I HAVE tried, at different times, to obtain pure chloride of barium for the purpose of determining its molecular combination with silver. The discordance in the results arrived at, with chloride made in different ways, prevented me from publishing my research. I worked in 1858 upon chloride of barium obtained in large quantities by the late M. Kuhlmann. I have prepared it myself from witherite. I found, then, that I could not entirely eliminate strontium and calcium from chloride of barium by the method of successive crystallisations. I succeeded no better by taking up the chloride of barium in boiling alcohol. Acting on Bunsen's advice, I took up the research again in 1863 and 1866, and again failed to arrive at concordant results, that is within the limits of accuracy possible when using alkaline chlorides. Having at last discovered the cause of the divergence in my results, I made another attempt to obtain pure chloride, but intended this time for quite a different purpose—that of ascertaining whether, by the action of heat, the barium spectrum could be changed into that of strontium, calcium, sodium, or lithium.

When I applied spectrum analysis to the research on the purity of barium compounds, I found that the chloride of barium obtained by successive crystallisations, however many times repeated, persistently showed a sodium spectrum, and that the carbonate obtained by precipitating this chloride by means of sesqui-carbonate of ammonium, persistently showed traces of the sodium and calcium spectra. The fact is that, by carrying on the operations in glass vessels, I was constantly attacking the constituents of the glass, and thus introduced silica, soda, and lime into the compounds formed. Having found the source of error, I was enabled to see in what direction to push my investigations.

I commenced with chloride of barium, prepared in large quantities by the late M. Kuhlmann, or made by myself by dissolving witherite in dilute hydrochloric acid. I first eliminated the iron, manganese, and lead in the chloride, by means of a slight excess of sulphhydrate of barium. Complete separation was effected when working in a solution kept boiling for from fifteen to twenty minutes. After filtration, the liquid, slightly

acidulated with hydrochloric acid, was concentrated to saturation, and then quickly cooled. The chloride was crystallised ten times, reserving the mother-liquor and the washings each time.

I treated this chloride five times with a 98 per cent solution of boiling alcohol. I found in the residue left after distilling the alcohol, besides barium, calcium, strontium, and sodium. The chloride, when put into a Bunsen flame on a platinum wire loop, gave it the sodium colour, and the sodium line continued visible so long as the residue from the decomposition remained in the flame.

To eliminate the silica contained in chloride thus treated, I had recourse to the method I employed for freeing the chlorides of calcium and strontium from silica,—that is to say, to the action of chloride of ammonium at a high temperature. I put it all, when dried by means of alcohol, into a platinum retort, and moistened it with a solution of pure chloride of ammonium. After desiccation, the mixture was heated till the greater part of the sal ammoniac was driven off. The chloride was taken up in just enough cold water to dissolve it, and the slightly clouded solution was filtered to separate the suspended silica.

I repeated the treatment with chloride of ammonium twice more, and on the third occasion the chloride, when dissolved in water, formed a perfectly clear liquid, leaving no trace of silica on the filter.

When this stage was reached, the solution was divided into two parts, A and B.

The part A, diluted with five times its volume of water, was poured into its own volume of water containing enough pure sulphuric acid to precipitate all the barium. The part B, also diluted with five times its volume of water, was poured into an equal volume of a dilute solution of sulphate and sesqui-carbonate of ammonium, in a covered platinum vessel, and containing enough sulphate to precipitate all the barium.

The barium, calcium, and strontium ought to be entirely in the form of sulphates in the A precipitate, whilst in the B precipitate—the barium only could be in the form of sulphate—the calcium and strontium ought to be found in the form of carbonates.

The sulphates, having been formed in very dilute liquids, were extremely finely divided, and remained in suspension a very long time. Their washing, which had to be done by decantation, occupied several months. The washing of the sulphate formed in the ammoniated medium was the most difficult, and took the longest time. It showed this peculiarity, that the washings, though quite clear, were clouded by the addition of a few drops of nitric acid, as though sulphate of barium was present, owing to the action of the sulphate of ammonium. But, whatever the cause of the fact might be, I frequently noticed it during the first washings.*

In the small residue left after evaporating the mother-liquors, and in the decantation water from both the precipitates A and B, I detected barium, calcium, strontium, and sodium.

After washing, I put the sulphate from A into a large platinum vessel; I moistened it with a saturated solution of sesqui-carbonate of ammonium, and left the solution to itself for twenty-four hours, sheltered from air-dust, to transform the calcium and strontium possibly still remaining in it into carbonates.

I diluted the sulphate from B with its own apparent volume of water containing 5 per cent of distilled hydrochloric acid, and I left this also to itself for twenty-four hours.

After this interval both the A and B sulphates were suspended in water, and left to settle. A very long time was required before this result was reached, and all the difficulties met with in the washings by decantation occurred again. I could find no other method of saving

* These researches were carried on in 1879; since that time sulphate of barium has been found to be soluble when precipitated in sulphate of ammonium.

time than by getting rid, at each washing, of a small part of the sulphate which had already been the cause of so much work.

After washing the precipitate from A, I treated it with water acidulated with hydrochloric acid, as I had done with the precipitate from B, and then washed it afresh with pure water.

The water acidulated with hydrochloric acid, which had held the sulphates of barium from A and B, contained barium and traces of calcium and strontium, and a great deal of sodium.

I kept the sulphates from A and B in suspension in boiling water in a platinum vessel, and however long they were kept in, and however often the water was renewed, the introduction of a portion from A and B into a Bunsen flame always had the initial effect of colouring the flame *yellow*. I had therefore to acknowledge that I was unable to free either of these sulphates of barium, most carefully and perseveringly treated, from sodium, so far that at the instant of contact it would not impart a yellow colour to a Bunsen flame or oxyhydrogen blowpipe. After trying the experiment sufficiently often in pure air, the sulphates were dried in the platinum vessels which held them, at first on a water-bath, and then at a high temperature. By the action of heat they were considerably contracted, remaining perfectly white. This effect can only be shown in platinum when never putting the metal into contact with water containing more than 5 per cent of its volume of hydrochloric acid.

Immediately after their desiccation, or after they had been kept under a bell-jar of pure air, kept dry by sulphuric acid, the sulphates imparted to flames a yellow colour, neither more intense nor more persistent than when moist. It follows, from these observations, that sodium combines with sulphate of barium in a still more marked degree than with the carbonates of calcium and strontium, and *at least* as strongly as with carbonate of lithium. But under the combined influence of heat and a current of gas, sodium can be eliminated with as much ease as the carbonates of calcium and strontium, and much more rapidly than carbonate of lithium.

Both sulphates, when freed from sodium in an oxyhydrogen blowpipe, imparted to this flame the green colour characteristic of barium compounds. When heated so far as to melt first, and then partially solidify by dissociation, they showed the well-known barium spectrum, as I describe in the next chapter. Neither at a low temperature, nor at the fusing-point of iridium, did they show any trace of the lines characteristic of the calcium, strontium, lithium, potassium, or sodium spectra.

In 1866 I reduced to sulphide some sulphate of barium obtained by the two methods I have just described. I effected this reduction by mixing the sulphates with pure petroleum black, and heating the mixture in a covered carbon crucible contained in a porcelain crucible, filled with charcoal that had been purified by hydrofluoric and hydrochloric acids.

Either on account of silica and soda from the fire having penetrated inside the crucible during the heating, or from some other unknown cause, the fact is that both sulphates showed a barium spectrum in an oxyhydrogen blowpipe with hydrogen in excess, in which the *sodium spectrum appeared continuously*.

I then reduced sulphate of barium by means of pure hydrogen. For this purpose I filled with sulphate a platinum boat, recently heated in a hydrogen and air blowpipe, contained in a large boat of pure carbon. I put this apparatus into a large porcelain tube, heated to a dull red heat, through which pure dry hydrogen had already been passing for some time. After the reduction I maintained the current of hydrogen until the tube was quite cold.

The sulphides were greyish white, excepting at the points of contact with the edge of the platinum boat. In an oxyhydrogen blowpipe, with hydrogen in excess, they

showed the same barium spectrum as the sulphates from which they were made, and in which the sodium spectrum was visible for some time, though it finally disappeared entirely.

In spite of the sulphide of barium attacking the platinum, I reduced, in a sheet of pure platinum shaped into a boat, a considerable quantity of sulphate, from which I had eliminated as far as possible all the sodium, in an oxyhydrogen blowpipe. Without withdrawing the boat containing the sulphide from the porcelain tube, I passed through it, at first in the *cold*, a current of pure and dry hydrochloric acid. When the greater part of the sulphide was thus transformed into chloride, I raised the tube to red heat, in the current, so as to make sure of having decomposed the whole of the sulphide of barium.

The chloride thus made, when introduced at once into an oxyhydrogen blowpipe, showed a very strong and brilliant barium spectrum, the same as that of the sulphate and sulphide, in which the sodium spectrum appeared *very temporarily*; this latter disappeared long before all the chloride was reduced to the state of oxychloride.

I dissolved in water a certain amount of the chloride thus made in platinum, in order to transform it into carbonate. This salt, obtained by double decomposition with the dilute solutions, being very difficult to wash, I hoped, as really was the case, to succeed more easily by passing a current of carbonic acid into a solution of ammonia containing chloride of barium. For this purpose I dissolved some ammonia in the solution of chloride of barium contained in a platinum dish, carelessly passing the gas through an *ordinary glass* tube, and, as soon as the liquid smelled strongly of ammonia, I passed into it a current of carbonic acid until all the barium was precipitated. The carbonate made thus was comparatively easy to wash; but after thoroughly washing it, and introducing it into a Bunsen flame or an oxyhydrogen blowpipe, it showed the sodium line *persistently*. The contact of ordinary glass with dissolved ammonia was sufficient to introduce into the salt a very small quantity of silicate of sodium, sufficient however, to render the complete elimination of this element almost impossible. I should add that, when dissolving silicate of sodium from the glass, it also combined with traces of calcium. I found that, at the fusing-point of iridium, spectrum analysis of an oxyhydrogen blowpipe showed transient, but distinct, traces of the blue calcium line, in addition to the barium and sodium spectra.

I might have omitted to mention the mistake I made; but I thought that the lesson it teaches might be useful to any person trying in the future to check these researches.

I was obliged, therefore, to re-commence the preparation of carbonate of barium in platinum, without using glass: this is very easy, because in default of platinum tubes to replace those of glass, one can use rubber or even gutta-percha tubes weighted with platinum, which have remained for some time in dilute hydrochloric acid, as I have done both before and since. Taking every precaution to protect it from air dust, I then precipitated an ammoniated solution of chloride made from sulphide, by means of carbonic acid. I washed the resultant carbonate of barium by decantation, first with cold water, then with boiling water, until the chlorine was entirely eliminated.

Immediately after the washing, the still moist carbonate, when introduced into a Bunsen flame, gave it very temporarily the sodic characteristics; but it was hardly brought to a bright red heat in an oxyhydrogen blowpipe before the sodium line disappeared, and was not afterwards visible, even at the fusing-point of iridium.

I treated this carbonate with water containing carbonic acid, but I was not able thus to weaken the slight sodic character it gave momentarily to an oxyhydrogen blowpipe flame.

After being dried in platinum, and kept for a long time

under a bell-jar protected from air dust, this carbonate showed a stronger sodium spectrum, but the sodium line faded very rapidly and left the barium spectrum only, when the air itself did not show any traces of the former.

(To be continued).

ON THE INVERSION OF SUGAR BY SALTS.*

By J. H. LONG.

It is a well-known fact that the specific rotation of solutions of cane-sugar is decreased by the presence of many neutral salts, even by sodium chloride and other salts of the alkali and earth groups. The amount of this decrease has been measured by several chemists, and recently very carefully by K. Farnsteiner (*Ber. d. Chem. Ges.*, xxiii., 3570), who has noted the connection between the molecular weights of the salts dissolved with the sugar and the amount of the depression they produced. In a solution containing for each part of sugar 3 parts of water and 10036 parts of sodium chloride the specific rotation dropped from 66.6° to 62.47° . Similar effects were observed in other cases.

The extent of this depression is dependent to some degree on the temperature, but a temporary increase in temperature does not permanently alter the rotation. In illustration, a solution of pure saccharose, containing in 100 c.c. 25 grms. of the sugar and 10 grms. of potassium nitrate, gave a specific rotation of $\alpha_D = 66.22^\circ$ at 20° . After heating one hour, but so as to avoid evaporation or pressure, the rotation was again determined, and found to be practically the same. The solution was heated in a small flask closed with a perforated rubber stopper, having a capillary glass tube in the perforation. It was possible by this means to heat the liquid to 100° in boiling water without risk of appreciable loss by evaporation.

On the other hand, a solution of sugar and zinc sulphate which gave a specific rotation of 64.98° when fresh, showed, after having been heated forty-five minutes in boiling water, as before, a specific rotation of 36.84° . In this case a decided inversion had taken place, as easily shown by other tests. The behaviour of zinc sulphate is similar to that of a large number of other substances. Loewenthal and Lensen (*Zsb. Chem.*, 1863, 120) and Ostwald ("Allg. Chemie," ii., 811) state that zinc sulphate and other neutral salts are without inverting action; but Béchamp, a little later (*Zsb. Chem.*, 1864, 573), and Gmelin ("Handbuch der Org. Chem." iv., 1, 691), gave a list of these salts which are able to produce a marked inversion. The phenomenon is an interesting one, and one which can now be easily explained, but until quite recently the literature has been almost silent on the subject. I wish to present in what follows a few observations bearing on the question.

Over a year ago, in giving instruction to a class of students on the use of the polarimeter, I suggested, as an illustration of a substance for examination, not-free from colour, the syrup of ferrous iodide of the pharmacopœia. Instead of exhibiting a more or less marked right-hand rotation, as was expected, it was found to be strongly levo-rotatory. The syrup, however, was known to be old, and had been exposed to the light. As a certain practical interest attaches to the question, it was decided to investigate fresh solutions.

The syrup of the pharmacopœia is made to contain in 100 c.c. about 63 grms. of sugar and 13.4 grms. of ferrous iodide. On January 19th, 1895, a litre of this solution was made according to the usual process, special care, however, being taken in the selection of the sugar and iodine employed. The liquid polarised immediately, in a 200 m.m. tube, gave $\alpha_D = 81.15^\circ$ at 20° . Four days later

the rotation was found practically unchanged, the syrup having been kept meanwhile in the dark. A bottle holding about 100 c.c., and furnished with a glass stopper, was then filled with the syrup and allowed to stand until May 6th, and exposed to diffused light. This portion now showed, on polarisation, $\alpha_D = 53.12^\circ$ in the 200 m.m. tube, while the original, kept in the dark, polarised 63.17° . On this date, May 6th, a second portion of the original was filled into a bottle and allowed to stand in the light. It was polarised at different intervals, with results as follows, at 20° , in the 100 m.m. tube:—

July 15th	α_D		+ 6.66°
Aug. 24th	"		- 4.36°
Oct. 22nd	"		- 13.10°
Nov. 15th	"		- 13.42°

Another portion of the original, which had stood since Jan. 19th in a small full bottle in the light, gave now, in the 100 m.m. tube, $\alpha_D = -15.66^\circ$. From this it appears that in the interval the saccharose had undergone complete inversion. The original rotation observed, 81.15° , was that of a solution in which some inversion had already taken place.

Another solution was prepared on May 9th, containing, in 250 c.c., 140 grms. of sugar and an amount of ferrous iodide corresponding to 28 grms. of iodine. The syrup and iodide solution were hot when mixed. This polarised at 20° gave a rotation of 33.25° in the 100 m.m. tube, which corresponds to a specific rotation of 59.38° . At intervals the following rotations were found from two portions of this solution, which had been poured into glass-stoppered bottles and kept in the light. One bottle was full and the other not quite full.

		Full bottle.	Partly filled.
July 13th	α_D	18.66°	+ 9.30°
Aug. 24th	"	8.58°	+ 3.56°
Oct. 22nd	"	3.76°	- 10.16°
Nov. 15th	"	2.70°	- 10.75°

It is apparent from the above that the presence of air in the bottle with the solution has a marked influence on the rapidity of inversion.

Influence of Temperature.

The solution just described stood at the laboratory temperature during the time of the observations. A marked decrease in the time required for full inversion would naturally be expected by working at a higher temperature. This was shown by heating some of the last solution in boiling water during ninety minutes. The solution was contained in a flask with a capillary stopper. Before heating it had a rotation of 33.25° in the 100 m.m. tube; after the application of heat the reading was -12.75° in the same tube. The following day the solution was re-heated through three hours and polarised again, giving now -13.00° at 20° . Heating through ninety minutes was therefore sufficient to complete the reaction, and it is evident that an inversion which, at the mean laboratory temperature of 20° to 25° , requires months for its completion, may be accomplished in less than two hours at the temperature of boiling water.

It was found later that a moderate increase of temperature does not greatly hasten the inversion; this becomes rapid only above 60° .

Influence of Light.

It should be remarked that the inversion by heat, as well as by long standing in the light, is accompanied by a decided loss of colour. A solution of ferrous iodide exposed to the air, or protected from the air and kept in the dark, soon becomes brown from partial decomposition and separation of iodine, which is easily shown by the starch reaction. In stoppered bottles in the light, however, this decomposition is almost wholly prevented, and in an already coloured solution in which free iodine is

* From the *Journal of the American Chemical Society*, vol. xviii., No. 2, February, 1896.

shown by tests the colour is lost by exposure to the light.

Well-made undecomposed solutions of ferrous iodide are described as light green, but they may become almost as colourless as water, leaving the iron in a perfectly reduced condition. It has been found, by numerous trials, that the rate of inversion is more rapid in bottles exposed to the light than in similarly filled bottles kept in the dark. The rapidity of inversion is further increased if the solution is exposed to the action of light and heat together. More will be said of this later.

The phenomena described above are not confined to ferrous iodide, but are exhibited by many other salts. In fact, from theoretical considerations, they should be expected in some degree from the salts of all the so-called heavy metals, as will presently be pointed out. First, however, some actual experimental results will be given.

Ferrous Chloride.

A solution containing, in 100 c.c., 50 grms. of cane-sugar and $4\frac{1}{2}$ grms. of pure ferrous chloride was prepared. The ferrous salt was made by the action of an excess of iron on hydrochloric acid, and the syrup made with this and the sugar was bright green. It showed a rotation of $32^{\circ}75'$ in the 100 m.m. tube, or a specific rotation of $65^{\circ}50'$. After heating one hour to 100° the rotation was found to be $-6^{\circ}42'$ in the same tube.

Ferrous Bromide.

The solution contained, in 100 c.c., 50 grms. of saccharose and 10 grms. of the bromide. The latter was made by the action of bromine and water on iron, and the solution so obtained was filtered into the dissolved sugar. The rotation of the fresh mixture was found to be $32^{\circ}25'$. A portion was heated one hour to 100° and was then polarised, after cooling to 20° , giving now a rotation of $-10^{\circ}26'$.

Ferrous Sulphate.

The solution of 100 c.c. was made with 50 grms. of sugar and 10 grms. of pure crystallised sulphate. It was slightly cloudy, and could not be polarised with the greatest accuracy, but the reading was nearly 33° . A portion was heated one hour away from the air. It became clear, and could be easily examined in the polarimeter, showing now, at 20° in the 100 m.m. tube, $18^{\circ}20'$. This decrease is much less than in the other cases, but not unexpected.

Ferrous Ammonium Sulphate.

The solution made contained, in 100 c.c., 50 grms. of sugar and 10 grms. of the crystallised salt. When fresh it gave a rotation of $33^{\circ}08'$. After heating five hours to 71° the rotation was found to be $27^{\circ}20'$. This solution was allowed to stand in a stoppered bottle in the light, and was polarised at different intervals with the following results:—

July 24th	a_D	..	..	$27^{\circ}20'$
Aug. 24th	"	..	..	$20^{\circ}22'$
Oct. 22nd	"	..	..	$10^{\circ}23'$
Nov. 15th	"	..	..	$7^{\circ}53'$

We have here, as before, a slow rate of inversion.

Manganous Chloride.

A solution was made on July 24th containing, in 100 c.c., 50 grms. of sugar and 10 grms. of the carefully purified salt, with $4H_2O$. It gave immediately a rotation of $32^{\circ}88'$, and, after heating five hours to 71° , a rotation of $28^{\circ}16'$. From this date, July 24th, the heated portion was allowed to stand in the light at the laboratory temperature in a full bottle, and showed at intervals the following rotations, all in the 100 m.m. tube, at 20° :—

Aug. 24th	a_D	..	..	$22^{\circ}20'$
Oct. 22nd	"	..	..	$4^{\circ}71'$
Nov. 15th	"	..	..	$1^{\circ}66'$

After standing a short time in the light this solution

became as colourless as water when observed in a clear glass bottle of 4 c.m. diameter.

Manganous Sulphate.

The experimental solution was made to contain, in 100 c.c., 50 grms. of sugar and 10 grms. of crystallised manganous sulphate ($MnSO_4 + 4H_2O$). The rotation was found to be $33^{\circ}16'$. On heating the solution one hour to 100° it became slightly decomposed and darker in colour, instead of lighter as with the chloride. The decomposition product was small in amount, but exceedingly fine and dark. It remained long in suspension, making an exact reading of the rotation impossible. It was about $+7^{\circ}$, however, in the 100 m.m. tube. The suspended substance was probably an oxide of manganese.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 27th, 1896.

Prof. CAREY FOSTER, Vice-President, in the Chair.

Prof. J. A. FLEMING read a paper on "The Edison Effect."

The Edison effect alluded to in the title of the paper is that, if a metal plate is placed inside the loop of an incandescent lamp, then a galvanometer, of which one terminal is connected to this metal plate and the other to the positive lead of the lamp, will indicate a current passing from the lead to the plate. If, however, the galvanometer is connected to the plate and the negative lead, no current passes.

Prof. Fleming, by connecting the poles of a condenser, —1st to the two leads, 2nd to the plate and positive lead, and 3rd to the plate and negative lead, in each case discharging the condenser through a galvanometer,—has shown that, after the lapse of a certain time, depending on the position of the plate, if the lamp is working at about four Watts per candle, the potential of the plate falls to that of the negative lead. If the plate, instead of being inside the loop of the filament, is outside, then the time taken by the plate to acquire the potential of the negative lead is considerably longer.

The space between the plate and the negative lead exhibits a kind of unilateral conductivity, for a battery having a low voltage is able to send a current from the plate to the negative lead, but not in the opposite direction. If, instead of using a cold metal plate, a second filament, maintained in a state of incandescence by an insulated battery, is used, then a current can be obtained between this filament and both the positive and negative leads.

If the voltage on the lamp is raised considerably above that required to give one candle-power for four Watts, then a current can be passed from the plate to the negative lead, while a galvanometer connected to the positive lead and the plate will indicate the passage of a current from the positive lead to the plate. When the lamp is in this condition, the space between the plate and the negative lead is very sensitive to the effects of a transverse magnetic field, such a magnetic field causing a large increase in the resistance.

The curve showing the connection between the current passing from the positive lead to the plate and the volts between the terminals of the lamp, is found to be discontinuous. As the volts are raised the current suddenly increases about tenfold, and it is while the lamp is in the condition corresponding to this upper portion of the curve that it is sensitive to the influence of the transverse magnetic field.

By using a movable plate it has been found that the minimum current is obtained when the plate is nearer the positive than the negative lead.

When an alternating current is used to supply the lamp, a continuous current can be obtained passing from the plate to either of the leads.

If a small platinum cylinder is placed surrounding each of the leads, then a current can be obtained between each of the cylinders and the positive lead, but no current between the two cylinders. The largest effect occurs when a cylinder near the end of the negative lead is connected to the positive lead.

The author considers that his experiments show that the resistance of a vacuum tube to the passage of a discharge would be greatly reduced if the kathode were made incandescent.

Prof. S. P. THOMPSON said he would like to have some information as to the state of exhaustion of the lamps; whether this was such as is found in ordinary commercial lamps, or whether it more nearly approached that used by Crookes. A great change in the conductivity, &c., took place at an exhaustion slightly greater than that ordinarily found in incandescent lamps. It would be of interest to vary the size of the kathode, and to investigate whether the magnitude of the effects observed depended on the fall of potential per unit length along the filament. Another point was whether the position of the plate for which the effect was a minimum was the same for all lamps, or whether it changed with the volts and the length of the filament employed. Again, did the minimum occur at a certain fraction of the distance between the positive and negative leads, or, as was the case in some of the phenomena observed by Crookes, at a definite distance from either of the leads? These points might be investigated by means of a lamp with a straight filament, where the fall of potential per unit length along the filament could be made the same as with the loop-shaped filament, but the fall of potential per unit length in the vacuum would be different. The author's proposed experiment of heating the kathode by concentrating on it the rays of a lamp did not seem to him (Prof. Thompson) to differ materially from Crookes's experiment in which an incandescent wire, heated by a current, was used as the kathode.

Mr. SKINNER said that the heating of the kathode by means of a "burning-glass" could easily be carried out.

Mr. BLAKESLEY pointed out that it would be quite possible to produce an increase of the current by means of a magnet.

Mr. SERLE said that Prof. J. J. Thomson had shown that a magnet affected the conductivity of a gas.

Prof. FLEMING, in his reply, said that no doubt the effects were largely dependent on the vacuum in the lamps. The lamps employed were exhausted to the ordinary commercial vacuum. Since it was found that the "treating" was more worn off the negative leg of the filament, and that a screen placed between the legs of the filament was more blackened on the side turned towards the negative leg, it would appear that the particles of carbon were shot off from the negative leg, and hence perhaps the charge was carried by these carbon molecules.

A paper of a purely mathematical character, entitled "Notes on the Electro-magnetic Effect of Moving Charges," by Mr. W. E. MORTON, was read by Mr. SERLE, who also made some remarks on his own investigations dealing with this subject.

The Society then adjourned till April 24th.

On the Röntgen Rays.—Ch. Girard and F. Bordas.—From the authors' experiments it seems to follow that the Röntgen rays emanate both from the kathode and the anode, and that the fluorescence produced on the wall of the Crookes tube acts but slightly upon sensitive plates.—*Comptes Rendus*, cxxii., No. 10.

NOTICES OF BOOKS.

Laboratory Tables for Qualitative Analysis. Drawn up by the Demonstrators in Chemistry of the Owens College. Manchester: J. E. Cornish. 1896.

THESE Tables belong to a class of publications in which the English press, during the last few years, has been sufficiently fertile. It goes without saying that the student will find here nothing erroneous. But it is, perhaps, no less true that he will encounter nothing which he might not find in works readily accessible.

The Tables are five in number, adapted for supervision on the wall of the laboratory, and treating respectively of the examination of solids, of preliminary examination for acids, and for organic substances; of the silver group, the copper group, with the arsenic group, the iron group under normal conditions, and in presence of organic, silicic, boric, hydrofluoric, and phosphoric acids; the barium group, and the magnesium group.

The thought again suggests itself to us—When will this wealth of elementary blossom ripen into a crop of discoveries?

Single-Salt Analysis. By B. P. LASCELLES, M.A., Assistant-Master at Harrow School. London: Swan Sonnenschein and Co., Ltd.

MUCH of what we have said concerning the Laboratory Tables drawn up by the Demonstrators in Chemistry at Owens College must apply also to this publication.

The student must always bear in mind that "single-salts" are not very commonly to be met with in nature or art, and that small quantities of impurities may modify—not to say mask—the reactions due to pure substances.

Repertory of Special Reagents, generally known under the Names of their Authors. ("Repertoire des Réactifs Spéciaux, généralement désignés sur leurs Noms d'Auteurs.") By FERDINAND JEAN (17, Faubourg St. Denis) and G. MERCIER (158, Rue Saint Jacques). Paris: Published and sold by the Authors. 1896.

THE number of special tests which have found their way into general practice is now very great, and they are generally mentioned simply under the names of their authors. Hence MM. Jean and Mercier have rendered an important service, not merely to students, but to analytical practitioners. In the work before us we find each reagent placed under the name of its discoverer, arranged in alphabetical order. The methods of preparing and applying the tests is given, and in many cases the extent of their sensitiveness. The special tests for strychnine, brucine, &c., have been overlooked, and in some cases the names of the authors are given incorrectly. Thus for Remsen we read here Rensen; for Runge we find Range; for Letheby, Lethebey; for Warrington, Warrigton; for Griess, Greiss; for Unverdorben, Anverdorben. &c.

We have the less scruple in calling the attention of MM. Jean and Mercier, because a second edition of so useful a book may be expected as a matter of certainty.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 10, March 9, 1896.

Certain Novel Properties of the Invisible Radiations Emitted by Phosphorescent Bodies.—Henri Becquerel.—This paper will be inserted *in extenso*.

Use of Artificial Hexagonal Blende as a Substitute for the Crookes Phials.—M. Troost—Already inserted.

Some Conditions which Govern Gaseous Combinations. Union of Oxygen and Hydrogen at Low Temperatures.—Armand Gautier and H. Helier.—A mixture of hydrogen and oxygen, after seventy-eight hours of contact, still contains about one-third of the explosive mixture uncombined. In glass tubes silvered within there ensues a total combination. Here, however, there is a secondary reaction at 450° to 480° , the silver combining with the glass and forming a triple silicate.

Yttrium and Thorium Carbides.—H. Moissan and M. Etard.—Yttria forms a carbide of the formula C_2Y . It occurs in transparent crystals decomposable by cold water, with formation of a gaseous mixture rich in acetylene, and containing methane, ethylene, and a small quantity of hydrogen. Thorium also forms a crystalline and transparent carbide, C_2Th , which is also decomposed by water, producing gaseous carbides, poorer in acetylene, but richer in free hydrogen.

Determination of the Mass of a Cubic Decimetre of Distilled Water, deprived of Air, at its Maximum Density.—J. Macé de Lépinay.—The mass of a cubic decimetre of water is 0.999954 kilo., with a possible error of 6 units of the last characteristic figure.

The rôle of the different Forms of Energy in Photography through Opaque Bodies.—R. Colson.—Already inserted.

Electric Effects of the Röntgen Rays.—Auguste Righi.

Some Facts relating to the Röntgen's Rays.—A. Batelli and A. Garbassa.—In a memoir published in the last number (January) of the *Nuovo Cimento*, we have pointed out that Röntgen rays may be obtained very brightly by rendering selected minerals fluorescent by means of the cathodic radiation. The use of Tesla's arrangement reduces the duration of the exposure. We have obtained good photographs with an exposure of two seconds only. We have indicated several substances which, on exposure to the Röntgen rays, give a fluorescence even more intense than that produced by barium platinocyanide. We have found that the time of exposure may be reduced by means of fluorescent substances placed behind the photographic plate. We have placed beyond doubt the existence of reflection and the absence of refraction.

Certain Specimens of Glass submitted to the Action of the X Rays.—V. Chabaud.—Already inserted.

Technics of Photography by the X Rays.—A. Imbert and H. Bertin-Sans.—This paper will be inserted in full.

On the Centres of Emission of the X Rays.—Prince B. Galitzin and M. de Karnojitzky.—A wood board is divided into squares, the sides of which are of 1 c.m. each; at each angle of the squares we introduce small nails of the same height. This board is placed upon a photographic plate contained in a wrapping impenetrable to ordinary light. Above the nails we arrange at a little distance Crookes tubes of various forms, tracing upon the wood the outlines of the tubes by means of a lead wire. An examination of the proofs thus obtained enables us to draw the following conclusions:—The surface of emission is very small. The centre of emission does not correspond to the surface of the tube, but is found in the interior at the distance of some millimetres from the side. It is quite possible that, beside the centre of emission corresponding to the cathode, there is another derived from the anode.

Direction of the X Rays.—Abel Buguet.—This paper will be inserted in full.

Thermochemical Study of the Amides and the Ammoniacal Salts of certain Chlorinated Acids.—Paul Rivals.—Not suitable for useful abridgment.

Photography in Colours. Substitution of Organic Colours for the Reduced Silver of Photographic Proofs.—Georges Adolphe Richard.—This memoir will be inserted as soon as possible.

Action of Nitrogen Peroxide and of Air upon Bismuth Chloride.—V. Thomas.—The compound obtained has a composition answering to the formula $BiOCl$.

Modifications introduced into the Methanometer ("Grisometer"), and on the Limit of Approximation which it can Reach.—J. Coquillion.—For small proportions of combustible gases this instrument is very accurate. The observer can obtain an approximation of $1/1000$ th.

Detection of Argon in the Natatory Bladder of Fishes and Physalæ.—Th. Schlösing, jun., and Jules Richard.—The presence of argon is shown in these gases, but it does not seem to play any perceptible part in the economy of these animals.

Determination of the Acidity of Pyroligneous Products.—M. Scheurer-Kestner.—The specimens of crude pyroligneous acid which the author has studied contain up to 17 per cent of their total acetic acid in the form of methyl acetate, and a quantity of phenolic compound corresponding to larger quantities of acetic acid.

Certain Derivatives of Triphenylsilicoprotane.—C. Combes.—Not suitable for useful abridgment.

Russian Oil of Aniseed.—G. Bouchardat and M. Tardy.—Russian oil of aniseed contains an enormous proportion of anethol, very small quantities of anisic anhydride, anisic acetone, anisic camphor, and various carbides of the formula $C_{30}H_{24}$. All these substances do not amount to more than the twentieth part of the anethol.

MISCELLANEOUS.

On the Combined Action of Light and Water in the Liberation of the Perfumes of Plants.—Eugene Mesnard.—It is light, and not oxygen as it has been assumed, which is the principal cause of the transformation and destruction of odorous substances, but in many cases these two agents seem to act in concert. The action of light makes itself felt in two different manners: on the one hand, it acts as a chemical power, capable of furnishing energy to all the transformations through which the odorous products pass from their elaboration to their total resinification; on the other hand, it exerts a mechanical action which plays an important part in the general life-history of plants; and this property explains the mode of the periodical liberation of the perfumes of flowers. The intensity of the perfume of a flower depends on the equilibrium which is established at every hour of the day between the pressure of water in their cellules, which tends to drive outwards the perfumes already elaborated contained in the epidermis, and the action of light which combats this turgescence. The whole physiology of perfumed plants flows from this simple notion. It is thus explained why in the countries of the East the flowers are less odoriferous than with us; why the trees, the fruits, even the vegetables, are sometimes filled with odoriferous products more or less resinified. It is also explained why in those countries the vegetation is thorny: the vegetation in those countries has too much light and too little water.—*Comptes Rendus*, cxxii., p. 493.

MEETINGS FOR THE WEEK.

WEDNESDAY, 8th.—Pharmaceutical, 8.30.

—Astronomical, 8.

FRIDAY, 10th.—Geologists' Association 8.

THE CHEMICAL NEWS.

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ON THE EFFECT OF THE RÖNTGEN X RAYS ON THE CONTACT ELECTRICITY OF METALS.*

By JAMES R. ERSKINE MURRAY, B.Sc.,
1851 Exhibition Scholar, Trinity College, Cambridge.

1. THE experiments described in this communication were made in the Cavendish Laboratory of the University of Cambridge, at Professor J. J. Thomson's suggestion, in order to find whether the contact potential of a pair of plates of different metals is in any way affected by the passage of the Röntgen "X" rays between the plates.

2. The vacuum bulb and induction coil for the production of the rays were enclosed in a box lined with metal, so that the plates and the apparatus used in measuring their contact potential difference should be screened from any direct electrical disturbances. At one

Hence the numerical value of the latter is simply that of the applied counter potential, but is of opposite sign.

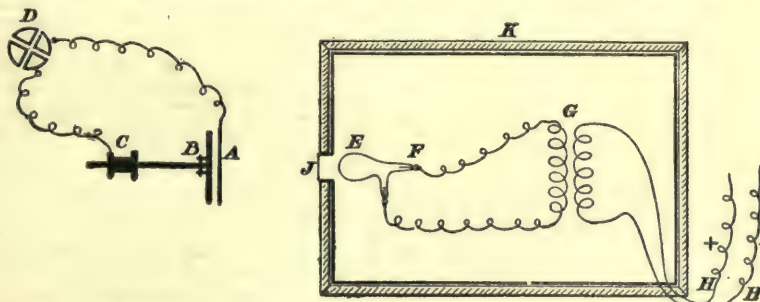
5. The plates were of zinc and tinfoil, the latter being mounted on thin ebonite to keep it flat. They were placed parallel to one another at a small distance apart, so that the rays fell perpendicularly on the back of the tinfoil plate, passed through it and the air space between them, and were absorbed by the zinc. The tinfoil plate was insulated and connected to the insulated quadrants of a Kelvin quadrant electrometer. The zinc was uninsulated, and was connected to the uninsulated quadrants of the electrometer. This plate is movable in a direction perpendicular to its plane, and can thus be drawn away from the tinfoil. If there is any electric potential difference between the opposing surfaces of the two plates, further separation causes a change in it which, reacting on the electrometer, deflects it.

6. When everything was in position, before starting the rays I measured the contact potential of the plates by the method mentioned above, and found it to be—

+0.44 volt,

the zinc being positive to the tinfoil. The rays were now turned on so as to pass through the tinfoil plate on to the zinc. The contact potential, measured while the rays were passing, was about—

+0.43 volt.



A. Tinfoil plate. B. Zinc plate, supported by a brass rod, which slides through the brass collar, C. D. Quadrant Electrometer. E. Vacuum tube. F. Negative electrode of tube. G. Induction coil. H, H. Wires connecting house battery to induction coil. J. Tinfoil screen—over the hole from which the rays issued—used in some experiments. K. Wooden box lined with sheet zinc.

side of the box there was a circular hole of about 3 cm. in diameter. The vacuum bulb was placed just inside this hole, and directed so that the rays should stream out through it in a direction perpendicular to the side of the box. In some experiments this hole was closed by a tinfoil screen, which allowed a large proportion of the rays to pass out while shutting in ordinary electrical disturbances. The plates whose contact potential difference was to be measured were placed at a short distance outside the box, in such a position that the rays could fall on them.

3. The diagram given above shows a plan of the principal parts of the apparatus, but omits the insulating supports and the subsidiary apparatus used in determining the contact potential by Lord Kelvin's null method. It is drawn roughly to scale, so as to show the relative dimensions and positions of the various parts.

4. To measure their contact potential I used the null method described by Lord Kelvin in his paper given to the British Association in 1880. I shall not describe this method in detail in the present communication, but may mention that the value of the contact potential is found by measuring the amount of the counter potential which has to be applied to the pair of plates to reduce the potential difference between their opposing surfaces to zero. The counter potential introduced to effect this annulment must obviously be equal and opposite to their contact potential difference.

But before the plates could be separated to see whether the counter potential applied had annulled the contact potential or not, the charge leaked away as if the insulation of the tinfoil plate were bad. Also I observed that when the plates were not in connection with one another, but only with the electrometer, they seemed to act as though they were connected together by a bad conductor or an electrolyte.

7. The X rays were now turned on so as to pass perpendicularly through the tinfoil plate on to the zinc. In a few minutes the deflection indicated—

—0.50 volt.

and remained steady there for several minutes. While in this condition I separated the plates. The deflection increased by a small amount, showing that the electrolytic power of the air while the rays are passing through it had somewhat more than counterbalanced the contact potential of the plates, and had established a slight difference of potential in the direction opposite to that which exists between the surfaces of the plates when connected metallically in air. This was confirmed by a measurement, made immediately after, by the null method, which gave—

+0.44 volt

for the potential difference between the plates; the rays not being on at the time.

8. In the experiments described above, the rays had fallen perpendicularly on the plates, passing through the

* A Paper read before the Royal Society,

tinfoil (see diagram). I now placed them so that the rays should pass between them in a direction approximately parallel to their surfaces. On breaking the metallic connection between the plates and turning on the rays the electrometer rose to—

—0.39 volt,

and remained steady there. Separating the plates produced no further deflection, which shows that the contact potential difference between the surfaces of the plates has been reduced to zero. This is confirmed by the measurement, made by the null method, of their contact potential which is now—

+0.39 volt.

9. In the above experiment the plates were at about 1 c.m. apart. I now increased the distance between them to 2, then to 5, and then to 10 c.m.; but in spite of the fact that in the last case the rays must have passed almost entirely through the air between the plates without striking on their surfaces, the electrometer always crept up from zero to —0.39 volt in a minute or two, and remained almost steady at that value.

10. In the above experiments there was no screen between the vacuum bulb and the ebonite back of the tinfoil plate. To make sure that none of the effects observed were due to ordinary electrical disturbances, I now placed a piece of tinfoil, in connection with the metal lining of the box containing bulb and coil, over the hole in the box from which the rays issued. With the plates parallel to the rays, and at about 1 c.m. apart, the electrometer rose while the rays were on from zero to —0.39 volt in two minutes, and remained steady there. This shows that the effects above described are due to the new rays, which can pass with ease through tinfoil, and not to the more ordinary forms of electric radiation.

11. In order to find whether these phenomena were strictly comparable with the results which Lord Kelvin had got many years ago by connecting the plates through an electrolyte, I made several experiments in which connection was made by a drop of acidulated water.

Before doing so, however, I measured their potential difference by the null method and found it to be—

+0.57 volt.

This variation from previous determinations is due no doubt to the influence of the atmosphere in tarnishing the plates. It is much less than the changes, due to that cause, which I have often found in other experiments on contact electricity. I now joined the plates by a drop of acidulated water while they were in connection with the electrometer only. The deflection at once rose from zero to—

—0.54 volt.

I now separated the plates, but this did not cause any notable change in the deflection, though it tended slightly in the direction which indicated that the contact potential of the plates had not been quite balanced by the electrolytic action. This is confirmed by the difference between 0.57 and —0.54 given above. After a short while the deflection fell to—

—0.48 volt,

which is nearly the value found previously for untarnished zinc and tinfoil in air, showing that the acidulated water has, in all probability, removed the tarnish, and is now balancing the contact potential between clean surfaces of the metals. The water was now removed, and the contact potential measured by the null method as before. It is still—

+0.57 volt,

for, of course, by far the greater part of the surfaces of the plates is still tarnished as before. In another experiment with a drop of acidulated water between the plates, I found that the contact potential was more than counter-balanced by the electrolytic action. This corresponds to the action of the rays mentioned in section 7,

12. It now occurred to me, that perhaps the electrolytic connection established between the plates when the rays were passing might be through the insulating supports of the tinfoil plate, and not through the air as I had hitherto supposed. To test the truth of this idea, several variations were made in the arrangements, all with a view to place the insulators in such a position that the rays could not reach them. First, I placed a screen of sheet zinc, with a hole in the middle of it, between the tinfoil plate and the hole in the box, from which the rays issue, so that the rays from the negative electrode of the vacuum bulb could fall only on the tinfoil plate and not on its insulating supports. These, by the way, consisted of pieces of good red sealing-wax, and under ordinary conditions, were excellent insulators. When the rays were started the electrometer moved from zero to a position which indicated a difference of potential as great as or greater than any which had been previously observed. This shows that the electrolytic connection had not been at all affected by screening the solid insulators.

This experiment was repeated several times, and in every case the result was the same. Still further confirmation of the aerial nature of the connection was obtained by a great alteration in the length and position of the insulating support. Instead of three short arches of sealing-wax, each made of one stick about 6 inches long, I used one tall one fully 12 inches high; one leg was attached to the wooden framework on which the uninsulated zinc plate was mounted, and the other, which was somewhat longer, held the tinfoil plate. The new insulator was thus one piece, about 24 inches long, of sealing-wax, with the greater part far removed from the rays, instead of six pieces each 3 inches long. A number of experiments were made with this arrangement. In all of them the potential varied under the influence of the rays by an amount similar in direction and magnitude to that previously observed.

13. I have observed that the activity of the vacuum bulb seems to determine, to some extent, the potential difference observed on the electrometer; that is to say, if the rays are very weak and unsteady (as judged by the fluorescence of the vacuum bulb) they do not make the air sufficiently electrolytic to counterbalance the contact potential difference between the surfaces of the plates. Thus, when the bulb is not fluorescing brightly and steadily, one gets results which are uncertain and perplexing. But these appear to give place in all cases to more definite values whenever the rays are strong and steady.

14. The conclusions I have drawn from these experiments are that (1) the influence of the rays on the zinc and tinfoil plates does not cause any direct or sudden change in their contact potential, but that (2) the air through which the rays pass is temporarily converted into an electrolyte, and when in this condition forms a connection between the plates which has the same properties as a drop of acidulated water, namely, it rapidly reduces the potential between the opposing surfaces of the plates to zero, and may even reverse it to a small extent.

It is interesting to note that this electrolytic property was found by Lord Kelvin ("Electrostatics and Magnetism," Art. xxiii., sections 412—414) to be possessed by the fumes from a burning spirit lamp. In both cases its cause is probably the same. It is, no doubt, due to a want of electrical equilibrium among, and a partial dissociation of, the molecules of the gas.

Constitution of Rhodinol.—Ph. Barbier and L. Bouveault.—The oxidation of the rhodinol of roses yields exactly the same results as that of the pelargonium compound. The two alcohols, $C_{10}H_{20}O$, extracted from the oil of pelargonium and from that of roses are identical. Rhodinol is a primary alcohol with an open chain having ethylenic connection, —*Comptes Rendus*, cxxii., No. 11.

ON THE INVISIBLE RADIATIONS EMITTED
BY THE SALTS OF URANIUM.

By HENRI BECQUEREL.

1. *Action on Electrified Bodies.*

In one of the last sittings of the Academy I announced that the invisible radiations emitted by salts of uranium have the property of discharging electrified bodies. I have continued the study of this phenomenon by means of the electroscope of Hurmuzescu, and I have been able to establish otherwise than I had previously done, photographically, that the radiations in question traverse various opaque bodies, in particular aluminium and copper. Platinum presents an absorption much more considerable than the two above-mentioned metals.

If we follow the progressive approximation of the gold leaves of the electroscope during the discharge, we observe that for deviations not exceeding 30° the angular variations are very decidedly proportional to the times, so that the speed of the approximation, or the fraction of a degree in which the gold leaves approach each other in a second, may give an idea of the relative intensities of the active radiations. I give here merely the numbers relating to the absorption through a plate of quartz perpendicular to the axis, and having a thickness of 5 m.m. The speeds are expressed in seconds of the arc and in seconds of time.

A lamella of the double uranyl and potassium sulphate placed below the gold leaves dissipates the charge of the electroscope with a speed represented by 22.50. The interposition of the plate of quartz reduced the speed to 5.43. The ratio of the two numbers is 4.15.

I have examined if the radiations emanating from the phosphorescent wall of a Crookes tube were enfeebled by the same plate of quartz in a proportion of the same order of magnitude. A Crookes tube was arranged at the exterior of the electroscope, opposite one of the faces of the lantern, for the glass of which had been substituted a plate of aluminium of 0.12 m.m. in thickness, and in front of this plate was placed a screen of copper with a circular perforation of 15 m.m. in diameter. The radiations through the copper are so much weakened that this effect may be neglected in the present experiment. When the Crookes tube was excited by an induction-coil, the gold leaves of the electroscope approached each other rapidly, —about 1° in 1.4 second, which corresponds to a speed of 257.4 expressed by means of the units adopted above.

When the quartz plate closed the circular aperture, the speed of the collapse of the gold leaves became 163.63, or 15.7 times smaller.

The enfeeblement is nearly four times greater in the second case than in the first, but it is of the same order of magnitude. This is the only point which this experiment manifests. The observation is not contrary to the probable hypothesis which ascribes the difference to the fact that the rays emitted by the uranium salt, and the rays emitted by the tube or by the phosphorescent glass, have not the same wave-lengths; but the different conditions of the two experiments do not enable us to assert this heterogeneity.

The electroscope has also enabled us to show the slight difference between the emission from a lamella of a uranium salt, which had been kept in the dark for eleven days, and the emission from the same lamella after it has been brightly illuminated with the magnesium light. In the former case the collapse of the leaves had a speed of 20.69, and after the luminous excitation it became 23.08.

We are ignorant what becomes of the electric charges thus dissipated, as also if the dielectrics were rendered conductors whilst traversed by these radiations. Experiment has shown that the crystalline lamella, if properly insulated, does not become charged even though it discharges the electrometer. Further, a lamella placed for a long time in presence of the apparatus does not communicate to it any charge.

2. *Emission of different Uranium Salts. Permanence. Excitation.*

If the phenomenon of the emission of invisible radiations which we have studied is a phenomenon of phosphorescence, we should be able to show the excitement by given radiations. This study is rendered very difficult by the prodigious permanence of the emission when the substances are kept in the dark secluded from luminous radiations, or from invisible radiations the nature of which we know. After more than fifteen days the salts of uranium still emit radiations almost as intense as on the first day. If we place on one and the same photographic plate, across black paper, a lamina which has been kept for a long time in the dark, and another which has just been exposed to the light of day, the impression of the silhouette of the second is a little stronger than that of the former. The magnesium light in these conditions produces merely an inappreciable effect. If we brightly illuminate the laminae of the double uranyl and potassium sulphate with the electric arc, or with the brilliant sparks from the discharge of a Leyden jar, the impressions are decidedly blacker. The phenomenon seems therefore to be a case of invisible phosphorescence, but which does not seem to be intimately mixed with visible phosphorescence or fluorescence. If, in fact, the uranium sesqui-salts are very fluorescent, it is known that the green uranous salts (the curious absorbent properties of which I have had the opportunity of studying) are neither phosphorescent nor fluorescent. But uranous sulphate behaves like uranic sulphate, and emits radiation as intense.

I will still mention another interesting experiment. We know that uranium nitrate ceases to be phosphorescent or fluorescent when it is in solution or melted in its water of crystallisation. I took a crystal of this salt, and after having placed it in a small tube closed with a thin plate of glass, I heated it in the dark, so as to avoid even the radiations of the alcohol lamp which supplied the heat. The salt was melted, and then allowed to crystallise in darkness, and I then placed it on a photographic plate covered with black paper, so as to preserve always the salt from the action of light. We might expect to observe no action, all luminous excitement having been avoided from the moment when the substance ceased to be phosphorescent, and yet the impression was as strong as that of salts exposed to the light, and even at points where the salt adheres to the plate of glass the impression was stronger than that of a specimen of uranium sulphate used for a comparative experiment on the same plate.

On this same photographic plate there were also crystals of uranium nitrate resting on laminae of glass with different surfaces, but the effects were sensibly the same.

I have also arranged uniform surfaces, formed of uranium sulphate and of double uranium-potassium sulphate, and I projected on these surfaces the spectrum of the arc through an apparatus of quartz. The bands of ultra-violet excitement were shown very definitely by fluorescence; but when I reproduced the silhouette of these surfaces upon a photographic plate, the silhouette became almost uniformly black, showing either that the specific emission of the substances marked the slight differences which might be observed for the different regions of excitation, or that the excitation did not take place in the region of the spectrum which was projected upon the surface studied.

3. *Absorption of different Substances.*

We may very easily study qualitatively the absorption of the radiation in question, by arranging on one and the same photographic plate sheets of these substances, or small flat tubes full of liquids, and covering them with a lamina of the double uranium-potassium sulphate, or any other uranium salt.

With these various substances used, in thickness

differing little from 2 m.m., I found that water is very transparent; the majority of the solutions, even those of metallic salts, solutions of copper nitrate, gold chloride, uranium nitrate, an alcoholic solution of chlorophyll proved moderately transparent. It was the same with paraffin and modeller's wax. Uranium glass was more opaque, as also a glass coloured red. Aluminium of this thickness is sparingly transparent; tin is more opaque, and a cobalt-blue glass appeared more opaque than the foregoing metals.

In another series of experiments I arranged different crystals and different optical combinations, intended to manifest the phenomena of double refraction and of polarisation. The images obtained were so feeble that I cannot at present give the results; still it was perceptible that quartz absorbs these invisible radiations more than does Iceland spar. Native sulphur behaved as if transparent.

The experiments in air and in rarefied air, which I mentioned at the end of my last paper, though not showing very signal differences, showed that proofs in rarefied air are a little stronger, which would manifest an absorption of air.

4. Refraction.

The facts which I mentioned in my last memoir have manifested refraction through glass. To these experiments we may add the following:—On one of the faces of a prism of crown glass, at a few m.m. from the edge, we fix, parallel to the latter, a small tube of very thin glass, of about 1 m.m. in diameter filled with crystallised uranium nitrate, and forming a linear source of emission of invisible radiations.

We then apply the other surface of the prism on a photographic plate. On developing the plate three days afterwards there was observed a diffused impression under the base of the prism; an impression separated from the trace of the edge by a white line, and the displacement of which is of the order of magnitude of that obtained under the same conditions for light. The considerable diminution of the luminous intensity when the sources of light are removed a little from the photographic plate has not allowed me hitherto to make measurements of the indices of refraction.

5. Anomalies presented by Different Substances.

The uranium salts emit invisible radiations with a remarkable permanency, but it is not the same with other phosphorescent substances.

I have obtained with calcium sulphide results of the order of those given by the salts of uranium, and I have mentioned in my last paper a proof of remarkable intensity obtained through 2 m.m. of aluminium. The same phosphorescent matter placed on a second photographic plate, under the same conditions, showed itself inactive, and since then I have not succeeded in obtaining any image with calcium sulphides. I have had the same want of success with specimens of hexagonal blende from different sources. I then sought to communicate a new activity to those substances by various known procedures, I have heated them in presence of the photographic plate without heating the latter, but I have not been able to obtain any impression.

In another series of experiments the various substances were refrigerated down to 20°, excited by daylight and by the magnesium light, but the magnesium salts alone yielded images.

Lastly, I have excited sulphides and hexagonal blende by the sparks from the discharge of a battery, and the substances, though rendered highly phosphorescent, still did not manifest any action through black paper. I have learned in the course of these experiments that our eminent colleague, M. Troost, has observed an analogous fact. Very old specimens of hexagonal blende which had at first yielded him energetic results have subsequently yielded results progressively decreasing, and are then

become inactive. There is here a very curious fact which may perhaps be explained by ulterior experiments.

M. L. Troost added the following observation on the foregoing paper:—

Our colleague, M. Becquerel, has observed that phosphorescent calcium sulphide, which in his earlier experiments acted very vividly on a silver gelatino-bromide plate, suddenly lost all its activity.

I have observed an analogous phenomenon with artificial hexagonal blende prepared by the apparent volatilisation of zinc sulphide in a very slow current of pure and dry hydrogen at a very high temperature.

This blende, the phosphorescence of which has been repeatedly excited by the magnesium flame, after having given for some time good proofs, produced afterwards paler and paler proofs, and finally nothing at all.

A new specimen, recently prepared, acted effectively under the conditions of my former experiments. On continuing this study I am about to verify if this activity will maintain itself or if it will disappear as in the former case.—*Comptes Rendus*, cxxii., p. 689.

THE STRUCTURE AND CONSTITUTION OF ALLOYS OF COPPER AND ZINC.

By GEORGES CHARPY.

In a paper submitted to the Academy in 1893, we indicated that the microscopic examination of the structure of brass may permit us to follow the modifications produced in this metal by treatment mechanical or chemical. Since that date we have examined in the same manner a great number of alloys of copper and zinc of various compositions and subjected to different treatments. The sum of these researches leads to the following conclusions:—

1. The alloys containing from 0 to 35 per cent of zinc all contain the same micrographic characters; the metal obtained by casting is formed by the agglomeration of long dendritic needles, the ramifications of which are often at right-angles. The dimensions of these crystallites depend chiefly on the speed of solidification of the metal. If we keep the metal at a temperature, high but below the point of fusion, the crystals develop, become more distinct, and finally pervade all the mass. They are then octahedra, presenting numerous macles, the dimensions of which are so much the greater as the metal has been raised to a higher temperature. We have not been able hitherto to effect the measurement of the angles of these crystals, but they seem to have identically the same form, and to constitute the totality of the mass as well in copper as in the alloy with 34 per cent of zinc, and all the intermediate alloys, which leads us to consider all these metals formed of isomorphous mixtures. For this group of metals there are hence two very definite structures; the one with dendritic crystals corresponds to fused metals; the other formed of very definite octahedral crystals corresponds to the state of perfect tempering. All cold hammering is recognised by the existence of deformed crystals, and all imperfect tempering by the appearance of small and ill-developed crystals.

When the proportion of zinc exceeds 34 per cent, the structure of the metal changes; the melted metal is formed of crystallites with rounded borders, and without dendritic ramifications; this structure is not appreciably developed by re-heating, and whatever may be the treatment undergone by the metal we have always two different substances—crystals entangled in a paste. When the proportion of zinc augments, these crystals become more rare, above 45 per cent the metal is formed of large plates with polygonal outlines which seem to have been developed around a certain number of centres of solidification, and in the interior of which we distinguish small crystals. When the proportion of zinc reaches 67 per cent, we have an alloy with a conchoidal fracture, and

which seems apparently homogeneous; but when the proportion of zinc becomes greater, potassa dissolves certain portions and shows ill-formed crystals which seem entangled in the zinc.

2. The observations relating to the microscopic structure enable us to interpret certain facts concerning the mechanical properties. In the alloys with a distinctly crystalline structure (from 0 to 34 per cent of zinc) the impurities are localised among the crystals. In the brasses of industry these impurities—which are almost always weak metals, lead or tin—form a solder which in the cold presents a great resistance. We find, in fact, that the malformations and the fractures are produced in the interior of the crystals, which explains why the fracture of these alloys formed of large crystals presents a very fine grain. But if we raise the temperature, the resistance of the solder decreases rapidly, and on passing 200° the metals become very fragile, the rupture taking place between the surfaces of the crystals. When the proportion of zinc is about 40 per cent, this effect is not produced; the crystals never occupy all the mass, and the impurities being distributed in a considerable mass do not weaken it so rapidly. It is known, in fact, that brasses containing from 36 to 45 per cent of zinc can be forged in heat.

3. The physical properties of the alloys of copper and zinc indicate plainly the existence of a definite compound, Cu_2Zn (67·3 per cent of zinc), which has been isolated by Le Chatelier. The researches of M. Riche on densities indicate likewise a perturbation in the neighbourhood of the alloy Cu_2Zn (34·5 per cent of zinc). On comparing these results with those furnished by microscopic study, we are led to put forward the following hypotheses on the constitution of the alloys of copper and zinc; alloys containing from 34·5 to 67·3 per cent of zinc must be mixtures in variable proportions of Cu_2Zn (a malleable compound) and of Cu_2Zn_2 (a hard brittle compound) approximating more or less, according to their composition, to the properties of the one or the other definite alloy. Lastly, the alloys containing more than 67·3 per cent of zinc will be mixtures of zinc with the compound CuZn_2 .—*Comptes Rendus*, cxxii., p. 670.

APPROXIMATE DETERMINATION OF THE VALUE OF CRUDE CRESOL.

By A. SCHNEIDER.

THE author founds his process upon a comparison of the intensity of the yellow colour assumed respectively by a pure cresol mixture and by cresols obtained from the substance under examination on treatment with nitric acid and ammonia. He first prepares a pure cresol mixture by dissolving crude cresol in soda-lye, diluting the solution with 5 vols. of water; the hydrocarbons (naphthalene, &c.) are removed by shaking out with benzene, and the cresols are separated by means of acid, the pyridines being combined at the same time. The cresols eliminated are collected, dried with calcium chloride, and distilled. Or we may use commercial cresol dehydrated by means of calcium chloride.

Of this pure cresol, 1 gram. is dissolved in water, and the solution is made up to 100 c.c. This solution serves as a standard for comparison.

One gram. of the cresol under examination is also dissolved to 100 c.c.; a knife-point full of powdered quicklime is added in order to seize upon any resinous matters which may be separated, and to increase the solubility of the cresols inclosed by the insoluble matters. We then take 1 c.c. of the solution of the crude cresol = 0·01 gram. of the substance, add 5 c.c. of dilute nitric acid, and heat on the water-bath for five minutes. The yellow liquid is then poured into a glass cylinder suitable for colorimetric comparisons, the rinsings are added, as also 10 c.c. of liquid ammonia, and the cylinder is filled up with water.

0·85 c.c. of the solution of the pure cresol (= 0·0085 gram. of pure cresol) are treated in the same manner, and the colours of the two solutions are compared. Of an official sample, the colour of 0·01 gram. crude cresol should not be weaker than that of 0·0085 gram. pure cresol.

The author assumes as the lowest percentage of an official sample 85 per cent of pure cresol, since cresols can take up as much as 12 per cent of water, and we may calculate on 3 per cent of other impurities. A high percentage of water is shown by the circumstance that such samples give with benzene a turbid mixture, whilst anhydrous samples form a clear mixture therewith.—*Zeitschrift Analytische Chemie*, xxxv., p. 115, and *Pharm. Central Halle*.

ANALYSIS OF A MIXTURE OF CHLORIDES, CHLORATES, AND PERCHLORATES.

By AD. CARNOT.

THE products of the ignition of chlorates may contain chlorates, perchlorates, and chlorides; they may contain hypochlorites. On the other hand, the products formed in the cold, or by the moist way, bleaching chlorides and hypochlorites, never contain perchlorates.

The examination of these two sorts of products constitute, therefore, two problems perfectly distinct in practice.

I shall here indicate the method for the analysis of the products of the dry way, mixtures of chlorides, chlorates, and perchlorates.

I first satisfied myself that the perchlorates do not undergo any reduction on the part of the reagents of the moist way which so readily transform the chlorates into chlorides, especially ferrous sulphate mentioned in a former paper, sulphuric acid, or zinc in presence of acids.

We may further effect the determination of the chlorate and of the chloride by one of the two following methods (A and B):—

A. We take two equal parts of the solution; in one we make directly the volumetric determination of the chloride, after the addition of nitric acid and of ferric sulphate, by means of an excess of silver nitrate and ammonium sulphocyanide; in the other, we effect the reduction of the chlorate by ferrous sulphate, and then continue, in the same liquid, to determine total chlorine. The first operation gives the chlorine of the chloride, and the second, by difference, the chlorine of the chlorate.

B. We operate upon one and the same portion of the liquid to be analysed. We determine the chloride by means of a standard solution of silver nitrate poured into the neutral liquid, after having added, as an indicator, a little sodium or potassium arseniate (in preference to potassium chromate, which has the inconvenience of acting on the reducing agent subsequently employed). Then we determine the chlorate by an addition of sulphurous acid and of ferrous sulphate in a known quantity, as directed in the former memoir. We may then calculate the chlorine of the chlorate and that of the chloride.

As for the perchlorate, it is determined by a special operation, and to that end it is reduced to the state of chloride in the dry way, since the moist way does not succeed.

It is difficult to obtain the complete reduction of the perchlorate in a crucible or in a glass tube without loss by volatilisation, although these procedures have been recommended. If we operate in a platinum crucible we observe a notable deficiency. If we make use of a test-tube we may judge from the white sublimate deposited at the mouth of the tube that there is great danger of loss. The melted chloride, besides, does not dissolve very readily.

But we may avoid all difficulty by a very simple expedient, which consists in mixing the saline powder to be

analysed with four or five times its weight of pure quartz sand, very fine, well washed, and dried.

We introduce the mixture at the bottom of a platinum crucible, and pour upon it sand enough to occupy a depth of 1 or 2 c.m. in the crucible, according to the quantity of matter to be treated. Experience shows that a depth of the layer of sand of 0.25 or even 0.5 c.m. does not entirely prevent all loss by volatilisation if we operate upon 0.500 gm. or 1 gm. of matter.

We heat over the Bunsen burner for twenty to thirty minutes, so that merely the bottom of the crucible is heated to redness. The chlorate and the perchlorate are thus entirely reduced, and if any chloride is volatilised it is condensed immediately on penetrating into the cooler and less permeable stratum of sand, the base of which is sometimes agglutinated for a thickness of several millimetres.

On treatment with water, all the chloride is dissolved in a few seconds. We filter and wash the sand with the greatest ease. Finally, in the neutral solution we determine the chlorine with a standard solution of silver nitrate, in presence of an alkaline chromate or arseniate.

This determination shows the proportion of *total chlorine*. That of the perchlorate is calculated by difference, deducting the proportion of the chlorate and the chloride, already ascertained by the foregoing experiments.

Five check experiments showed discrepancies of less than 0.5 m.-gram. — *Comptes Rendus*, cxxii., p. 452.

ON A

NEW ELEMENT PRESENT IN THE RARE EARTHS CONTIGUOUS TO SAMARIUM.

By EUG. DEMARÇAY.

It is well known that Marignac obtained, by fractionating, earths contiguous to samarium, having sparingly soluble potassium sulphates, an earth which he named at first *Y_a*, and then gadolinium, after Lecoq de Boisbaudran had characterised it more definitely by its peculiar spectrum. On fractionating by crystallisation from fuming nitric acid (sp. gr. = 1.45) the portion of the rare earths rich in samarium, I separated at first a colourless nitrate, sparingly soluble in the cold, and giving only feeble traces of the absorption-bands of samarium, and showing with the spark a very fine and rich spectrum of gadolinium, then more soluble fractions, becoming more and more yellow up to portions of an orange-yellow, and very intense.

These latter afford a fine line spectrum, without any traces of the rays or the bands of gadolinium. If we examine the inner fractions with the spark, we see the strong rays of gadolinium become weaker in proportion as the nitrates become more soluble, and, inversely, the very feeble rays of samarium become stronger.

But along with the latter there are others of a medium intensity in the first spectrum, which are strengthened at first so as to reach their maximum lustre, whilst the rays of gadolinium are enfeebled, and those of samarium are not yet very strong, and diminish further in intensity until they appear only very faintly in the purest samarium which I possess as yet.

We are therefore obliged to admit the presence of a peculiar nitrate, more soluble in strong nitric acid than that of gadolinium, and less than that of samarium. The earth obtained from this nitrate differs from the rare earths already known:—

1. By its colourless salts without an absorption spectrum.
2. It is colourless, which distinguishes it from terbia.
3. It differs by its spectrum from the oxides of lanthanum, cerium, gadolinium, ytterbium, and terbium, the only rare earths yet known with colourless salts.

It is, further, very distinct from the oxides of lanthanum and cerium by its relatively feeble basicity and the relative solubility of its double potassium sulphate; from ytterbia, by its relatively strong basicity and the slight solubility of its double sulphate; but it approximates much to gadolinia and samaria, from which it is distinguished by its spectrum. I shall designate provisionally, until I have succeeded in isolating it in a greater state of purity, the radicle of this earth as Σ , and the earth itself as Σ_2O_3 .

Besides Σ_2O_3 we may suspect the presence of another earth. If, in fact, we carefully compare the spectra of gadolinium and of Σ , we find the rays of the former stronger in the first spectrum than in the second; there are others approximately as strong in the one as in the other, and which may belong to a third element. I do not wish to insist on this doubtful point, which particular circumstances may explain otherwise, and I content myself with mentioning some strong rays which seem to me to belong respectively to gadolinium and to Σ . Among the rays of the latter I mention, as the most characteristic, 4228.1, 4205.9, 4128.4, 3972.2, 3930.8, 3819.9; among those of gadolinium we remark, especially, 4263.1, 4178.2, 4098.6, 4063.4, 4049.9, 3959.9, 3958.1, 3916.7, 3852.6, 3850.9, 3549.3, 3545.7.

I have been able to satisfy myself, thanks to the kindness of Lecoq de Boisbaudran, that none of the foregoing rays can be ascribed to terbium. He has kindly placed at my disposal a specimen of his purest gadolinia, the result of prolonged fractionations of Marignac's sample (already very rich); on the other hand, a terbia of a very deep chocolate-brown, the fruit of beautiful researches, which have led among other discoveries to that of dysprosium. I have examined their spectrum, and found that Σ only occurs there incidentally.

I am indebted to the same *savant* for the opportunity of having been able to examine a samaria prepared by Prof. Clève, and which is considered as one of the purest hitherto obtained. The earth of the illustrious Swedish *savant* contained no terbia, and little gadolinia, but it should contain a considerable proportion of Σ . Hence I conclude that the atomic weight of samarium should certainly be changed, and probably reduced below 150, the figure now received. — *Comptes Rendus*, cxxii., p. 728.

THE COMPOSITION OF WATER. A SHORT BIBLIOGRAPHY.

By T. C. WARRINGTON, B.A.

(Continued from p. 157).

C. Combination of a Weighed Quantity of Hydrogen with Oxygen to form a Weighed Quantity of Water.

(41). 1870. JULIUS THOMSEN.

"Ueber einige Constanten des Wasserstoffs und des Sauerstoffs."

Ber., (1870), iii., p. 927.

A short account of one experiment is given.

(42). 1886. J. D. VAN DER PLAATS.

"Essai de Calcul des Poids Atomiques de M. Stas."

Ann. Chim. et Phys., (1886), [6], vii., p. 499.

In a note on p. 529 of the paper is given the result of one experiment by the author. On the same page is discussed the value for H ($O=16$) from Stas's determination of molecular weight of NH_4Cl and NH_4Br .

(43). 1887. E. H. KEISER.

"Ueber die Verbrennung abgewogener Mengen von Wasserstoff und über das Atomgewicht des Sauerstoffs."

Ber., (1887), xx., p. 2323.
Abs. J. C. S., (1887), lii., p. 1078.
Beibl. Wied. Ann., (1887), xi., p. 743.

Preliminary notice.

(44). 1888. COOKE and RICHARDS.

"The Relative Values of the Atomic Weights of Hydrogen and Oxygen."

Amer. Chem. J., (1888), x., p. 81.
Proc. Amer. Acad., (1888), xxiii., [N.S. xv.], p. 149.
Abs. J. C. S., (1888), liv., p. 647.
Beibl. Wied. Ann., (1888), xii., p. 411.

The paper discusses bearing of Prout's hypothesis, and gives a critical account of previous work. The special feature of the author's procedure is that hydrogen is weighed in a large globe and driven over copper oxide by nitrogen, the ratio $H_2 : H_2O$ being thus obtained.

(45). 1888. COOKE and RICHARDS.

"Additional Note on the Relative Values of the Atomic Weights of Hydrogen and Oxygen."

Amer. Chem. J. (1888), x., p. 191.
Proc. Amer. Acad., (1888), xxiii., p. 182.
Abs. J. C. S., (1889), lvi., p. 910.
Beibl. Wied. Ann., (1888), xii., p. 732.

The object of the note is to apply a correction for the shrinkage of the balloon suggested by Rayleigh's works.

(46). 1888. E. H. KEISER.

"On the Combustion of Weighed Quantities of Hydrogen and the Atomic Weight of Oxygen."

Amer. Chem. J., (1888), x., p. 249.
Beibl. Wied. Ann., (1888), xii., p. 733.

Palladium was used to condense and weigh hydrogen, which was then passed over heated copper oxide and the water weighed.

(47). 1889. W. A. NOYES.

"On the Atomic Weight of Oxygen."

Amer. Chem. J., (1889), xi., p. 155.
Chem. News, (1889), lix., p. 244.
Abs. J. C. S., (1889), lvi., p. 672.
Beibl. Wied. Ann., (1889), xiii., p. 585.

Hydrogen is led into an apparatus containing a weighed amount of hot copper oxide. The increase in weight gives the weight of hydrogen. The apparatus is then exhausted of water and again weighed to obtain the weight of water formed.

(48). 1889. G. STILLINGFLEET JOHNSON.

"Note on the Method of Determining the Atomic Weight of Oxygen adopted by W. A. Noyes."

Chem. News, (1889), lix., p. 272.
Abs. J. C. S., (1889), lvi., p. 935.
Beibl. Wied. Ann., (1889), xiii., p. 842.

The errors from occlusion, the presence of sulphur in copper, &c., pointed out.

(49). 1890. W. A. NOYES.

"The Atomic Weight of Oxygen."

Amer. Chem. J., (1890), xii., p. 441.
Proc. Amer. Ass., (1890), xxxix., p. 167.
Abs. J. C. S., (1890), lviii., p. 1370.
Nature, (1890), xlii., p. 530.

The author corrects and extends his former results.

(50). 1891. W. A. NOYES.

"The Atomic Weight of Oxygen."

Amer. Chem. J., (1891), xiii., p. 354.
Abs. J. C. S., (1891), lx., p. 1154.

The paper consists of a rejoinder to Keiser (29).

(D). Indirectly from the Molecular Weight of Ammonium Chloride.

(51). 1860-1882. J. S. STAS.

"Recherches sur les Rapports réciproques des Poids Atomiques."

Bull. de l'Acad. Belgique, (1860), x., p. 294.

"Nouvelles Recherches sur les Lois des Proportions Chimiques."

Mém. de l'Acad. Belgique, (1865), xxxv., pp. 48-58.

"Du Rapport Proportionnel entre l'Argent, les Chlorures, et les Bromures."

Mém. de l'Acad. Belgique, (1882), xliii., p. 62.

Stas determines the relation of Ag to NH_4Cl and NH_4Br , and so the molecular weight of these substances. Then the molecular weights of nitrogen, chlorine, and bromine being otherwise accurately determined, the atomic weight of hydrogen, compared with $O = 16$, can be found.

(52). 1894. J. THOMSEN.

"Experimentelle Untersuchungen zur Feststellung des Verhältnisses zwischen den Atomgewichten des Sauerstoffs und Wasserstoffs."

Zeit. Phys. Chem., (1894), xiii., p. 398.

Beibl. Wied. Ann., (1894), xviii., p. 809.

The author finds the quantity of ammonia gas requisite to saturate a given weight of hydrochloric acid. Then atomic weights of nitrogen and chlorine being known, the atomic weight of hydrogen ($O = 16$) may be calculated.

(53). 1894. MEYER and SEUBERT.

"Ueber das Verhältniss der Atomgewichte des Wasserstoffs und des Sauerstoffs."

Ber., (1894), xxvii., p. 2770.

Beibl. Wied. Ann., (1895), xix., p. 226.

Criticism of J. Thomsen's method (51).

(To be continued.)

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 161).

CHAPTER X.

THE CHARACTERS IMPARTED TO FLAMES AND TO THE ELECTRIC SPARK DISCHARGE AND ARC BY BARIUM COMPOUNDS.

The Luminous Spectra of Barium.—Compounds of barium impart to colourless flames, and to electric sparks and discharges, a greenish yellow tint. The green tint is stronger when the compounds are free from sodium. An electric arc charged with baryta is *white*. Spectrum analysis of flames charged with baryta shows a spectrum with very numerous and varied bands. I did not like to acknowledge myself beaten, considering the question I was investigating, viz., whether, by increasing the temperature of flames or the intensity of electric phenomena, it was possible to cause the appearance of lines characteristic of sodium, potassium, lithium, calcium, or strontium, when the compounds of barium were previously freed, by means of chemical and physical forces, from the slightest trace of these metals.

For carrying on this investigation I employed sulphate of barium made by two different processes, sulphide made from these sulphates, and oxide made in an oxyhydrogen blowpipe from carbonate and chloride of barium prepared from sulphide.

In the last chapter I described in detail the methods by which I prepared these compounds.

No matter what the source of the barium might be, its spectrum, in an oxyhydrogen blowpipe at the highest possible temperature, was always the same.

When it was derived from sulphate prepared by either method, but in a medium free from silica and as much as possible from sodium, as is the case with chloride crystallised ten times in succession in platinum, and then heated several times in platinum to a dull red heat with chloride of ammonium, and taken up each time in pure water, I found the following facts:—

Sulphate, when dried protected from air dust, and heated on a sheet of platinum free from sodium, immediately coloured *pure yellow* an oxyhydrogen blowpipe burning with a large excess of hydrogen. On regulating the temperature so as to dry the sulphate only without fusing it, it was noticed that after a short time the yellow colour disappeared from the blowpipe, and was replaced by a pale greenish yellow at first, and afterwards by a *deep green* colour. After having sufficiently renewed the layers of simply dried sulphate, spectrum analysis of the flame showed that the sodium line gradually faded, until it reached the state in which it was seen in a blowpipe burning in the surrounding air.

By taking great care, it is possible to bring the sulphate to a condition in which it no longer shows traces of the sodium line, even before it is heated enough to melt it in small *clear, transparent, and colourless* drops, which remain on the surface of the dried sulphate like dew, having the appearance, on cooling, of white enamel.

I succeeded, on several occasions, in eliminating the sodium which is firmly held by the sulphate, and using salt from two different sources, and I got the best result when separating, as I did the night before with carbonate of strontium, nearly all the sodium, and then completing the reaction in a carefully washed room and in still air.

When two persons are engaged in carrying on this delicate work,—one being engaged in volatilising the compound by suitably adjusting the blowpipe, and the other in examining the spectrum formed,—one is very soon convinced that there is no connection between the sodium line and the yellow barium lines, in spite of their proximity when a spectroscopic of low dispersive power is used. When the precaution is taken of volatilising at least *two-thirds* of the sulphate experimented upon, no matter what the temperature of the sulphate, or rather the products of its dissociation, may be, and when a Duboscq spectroscopic with three prisms is used, it is impossible to cause the appearance of a line corresponding to either *one or other of the double sodium line in the solar spectrum taken as a standard*.

It is impossible to produce a trace of sodium from sulphate of barium by raising the temperature.

There can be no possible doubt on this point. As regards the spectrum of sulphate of barium, and the products of its dissociation, my observations have yielded the following results:—

The Flame Spectrum of Sulphate of Barium.—Sulphate, when entirely freed from sodium and heated in an oxyhydrogen blowpipe to a temperature below that at which the diffuse greenish line, at 82.2 on the Steinheil and 90 on the Bunsen spectroscopic, appears, shows a spectrum consisting entirely of the red, orange, and green bands, made familiar to us by Bunsen's and Kirchhoff's work. When the temperature is high enough to show the greenish blue line, the bands show a tendency to better definition, but I cannot say that I have succeeded in seeing a single sharp line in the spectrum, not even the greenish blue line above mentioned.

The position of the bands was *remarkably constant*; I ascertained the position to be the same as described by Bunsen, in his "Spectral Analytische Untersuchungen," for the flame spectrum of chloride of barium, within the limits of error of measurement, i. e., 0.50 division on the micrometer.

On raising the temperature, so as to colour the oxyhydrogen flame quite blue with incandescent hydrogen, the appearance of the spectrum changes and it becomes intensely brilliant. The bands at 59.75 to 61.80, and 85.2 on the Steinheil spectroscopic, corresponding to 61 to 63, and 90 on the Bunsen spectroscopic, tend to resolve into lines; they still, however, remain hazy. In the middle of the interval between E δ and F, there appears a band which, at the point of greatest brilliancy, is seen to consist of a *group* of extremely fine *green lines*. These green lines, the number of which varies with the temperature, occupy six and a half divisions on the micrometer; they are situated between 75.5 and 82 on the Steinheil spectroscopic, corresponding to from 79 to 86 on the Bunsen scale. This complex group is drawn on the accurate illustration of the flame spectrum of chloride of barium given by Roscoe. When using the Duboscq instrument with three flint glass prisms, I tried to determine accurately the position of each of these lines, but did not succeed. The absorption of light was so great that I could only just see the lines.

I tried again with the Hilger instrument with three Iceland spar prisms, but with no better success.

Whatever the reason may be, the appearance of the spectrum of sulphate of barium, and the products of its dissociation, varies, according as it is examined in the part of the oxyhydrogen blowpipe where the hydrogen is or is not incandescent. In the first case the spectrum drawn by Roscoe, in the second case that described by Bunsen, is seen. But in neither case is there seen any trace of the characteristic spectra of potassium, lithium, calcium, or strontium.

As regards calcium and strontium, I specially directed my attention to finding out whether, *during or after* the dissociation of the sulphate and when the temperature was at its highest (the fusing-point of iridium), the appearance of the spectrum changed, and especially whether the blue calcium line at 125.5 and the blue strontium line at 99.0 on the Steinheil spectroscopic, corresponding to 135.0 and from 105 to 106 on the Bunsen instrument, appeared even momentarily, as I found they did when I purposely mixed with the sulphate of barium about 1/10,000th part of the sulphates of calcium and strontium.

I was not able to detect the blue calcium and strontium lines. I call special attention to the blue calcium line at 125.5 on the Steinheil spectroscopic, and not the green calcium band from 60 to 61.5, because the flame spectrum of sulphate of barium, when quite free from sulphate of calcium, has a *green line at the same place when measured in the Steinheil spectroscopic*. When using the large Hilger instead of the Steinheil spectroscopic, it is readily seen that there is, between the green barium and the green calcium lines, a distance equal to about *three times* the width of the lines. The coincidence in the position of the green barium and calcium lines, noted by spectroscopists, must be due to a want of dispersive power in the instruments used by those observers. My numerous researches, at different times, to satisfy myself as to the purity of sulphate of barium, have led me several times to undertake the spectrum analysis of an oxyhydrogen blowpipe charged with this compound, both at the lowest and highest possible temperatures, and the results have always been the same when I had succeeded in previously eliminating the calcium and strontium so firmly combined with barium.

The Flame Spectrum of Sulphide of Barium.—As I described in the last chapter, I converted pure sulphate of barium, free from sodium, into sulphide, both by means of hydrogen in platinum, and by means of petroleum black, in a pure carbon crucible.

The sulphide made by means of hydrogen in platinum, when volatilised in oxyhydrogen gas with an excess of hydrogen, showed on spectrum analysis, at corresponding temperatures, the same spectra as those of pure sulphate in an oxyhydrogen flame. The bands in these spectra are as constant in position as those of the sulphate.

Moreover, I found analytically that, in an oxyhydrogen blowpipe with an excess of hydrogen, the sulphide of barium was quickly reduced to the form of a mixture of oxide and sulphate of barium.

The Flame Spectrum of Chloride made from Sulphide of Barium.—After having reduced the sulphate free from sodium in platinum, by means of hydrogen, I transformed the resulting sulphide into chloride. This reaction was effected, protected from draughts, by means of the very purest hydrochloric acid, and without withdrawing the platinum boat containing the sulphide from the porcelain tube. The chloride thus formed, when heated at once in an oxyhydrogen blowpipe with an excess of hydrogen, showed, at a temperature below that of incandescent hydrogen, the barium spectrum with the well-known *nebulous* bands, and, at a temperature approaching the fusing-point of iridium, after transforming the chloride into oxide, a spectrum composed solely of well-defined bands, but without *lines* properly so-called, not even the line at $82^{\circ}2$ on the Steinheil, or go on the Bunsen, spectroscope.

I saw a very faint sodium line at the commencement of the heating; but long before the chloride was transformed into oxide, I was not able to see the sodium line any more distinctly than in air at the same time.

The Flame Spectrum of Carbonate of Barium.—Wishing to study the flame spectrum of carbonate of barium, and of the oxide made from it, I prepared some carbonate from pure chloride, as described in the last chapter.

Although I mentioned at some length, in the last chapter, the necessity for effecting the precipitation of chloride by means of sesqui-carbonate of ammonium in platinum, as well as all the washings of carbonate of barium, and of entirely avoiding the use of glass, I think I ought to emphasize the point, so as to leave no doubt whatever to anyone who may attempt this operation in glass vessels. By neglecting this precaution, silica, calcium, and sodium from the glass are introduced, and the resulting carbonate of barium—when introduced into an oxyhydrogen blowpipe in which the hydrogen is incandescent—shows, on spectrum analysis, a permanent sodium line, and even the blue calcium line at 135 on the Bunsen spectroscope.

The results of these observations on carbonate of barium apply therefore to a salt prepared exclusively in platinum.

Carbonate made and kept protected from air dust, when heated in an oxyhydrogen blowpipe, gave it a very fleeting yellow colour. When the temperature was raised to bright red, and the layers of the salt were properly renewed, the sodium spectrum disappeared long before the decarbonisation was effected. This result being attained, the barium spectrum appeared with or without a faint sodium line, according to the state of the air. At a similar, but comparatively low, temperature, carbonate imparted to an oxyhydrogen blowpipe a paler green colour than that imparted by sulphate of barium: the spectrum of carbonate was also fainter and less distinct than that of sulphate; it consisted, like the latter, entirely of bands. At the fusing-point of platinum the bands became sharper, but did not resolve into lines. When the fusing-point of iridium was approached, the original bands were still seen, but the band from $75^{\circ}5$ to 82 on the Steinheil, or from 79 to 86 on the Bunsen, spectroscope, was resolved into the group of *very fine* green lines which I mentioned above in connection with the spectrum of sulphate and the products of its dissociation. Moreover, at this high temperature carbonate ought to be entirely dissociated. I am therefore justified in saying that the spectra of carbonate and the products of its dissociation are identical with those of sulphate and the products of its dissociation. To recapitulate, these spectra have nothing in common with the spectra of sodium, potassium, lithium, calcium, or strontium.

(To be continued).

ON THE INVERSION OF SUGAR BY SALTS.*

By J. H. LONG.

(Concluded from p. 162).

Zinc Sulphate.

A SOLUTION containing 50 grms. of sugar and 10 grms. of the sulphate in 100 c.c. showed, when fresh, a rotation of $32^{\circ}98'$ for 100 m.m. After heating forty-five minutes in boiling water, the rotation was reduced to $18^{\circ}42'$ for the same tube.

Potassium Aluminum Sulphate.

With a solution containing 50 grms. of sugar and 5 grms. of the alum in 100 c.c. a rotation of 33° was found immediately. A portion was heated one hour in the water-bath to 100° , and on cooling to 20° was polarised again, showing now a rotation of $-9^{\circ}99'$. The heated solution became slightly cloudy, but the original remained clear through the several weeks it was kept.

Lead Nitrate.

A fresh solution with 50 grms. of sugar and 10 grms. of the salt in 100 c.c. showed a rotation of $33^{\circ}13'$. A portion, heated one hour to 100° , showed, after cooling to 20° , a rotation of $-9^{\circ}65'$ in the same tube.

Lead Chloride.

Some chloride was made by precipitation of the nitrate by sodium chloride. The product was re-crystallised from hot water, and washed repeatedly on a filter with cold water. About 2 grms. of the moist precipitate was mixed with 50 grms. of sugar in water enough to make 90 c.c., and heated until it dissolved. On cooling, the volume was made to 100 c.c. A part of the chloride separated. The rotation was now found to be $23^{\circ}52'$. The mixture was shaken, and a portion transferred to a flask with capillary stopper, where it was heated one hour to 100° . After cooling, the rotation was found to be $-7^{\circ}53'$.

Cadmium Chloride.

A fresh solution with 50 grms. of sugar and 8 grms. of the chloride in 100 c.c. gave a rotation of $32^{\circ}91'$. After heating to 100° it was reduced to $-9^{\circ}50'$.

Mercuric Chloride.

The original solution of 50 grms. of sugar and 5 grms. of chloride in 100 c.c. gave a rotation of $33^{\circ}22'$. A portion was heated an hour to 100° and became turbid, depositing on cooling a fine white precipitate. The clear liquid showed a rotation of $-10^{\circ}80'$. A second portion was heated a shorter time, to the beginning of turbidity only. It was quickly cooled and polarised, showing a rotation of $-4^{\circ}82'$. By prolonged heating more of the precipitate is formed. It appears to consist of mercurous chloride only.

The salts tested above, while commonly called neutral, are those in which the base is very weak when compared with the acid. It is such salts that show in solution an acid reaction with certain indicators, and the parallelism between the phenomena observed here and that of the inversion of sugar by acids naturally suggested itself. The following further test with a solution of ferrous iodide was therefore made:—This solution contained, in 100 c.c., 50 grms. of sugar and 10 grms. of the iodide. It polarised when fresh $32^{\circ}41'$ in the 100 m.m. tube. A number of small phials were nearly filled with this solution, and they were heated in a thermostat through different times, as shown below. The phials were made of selected glass, not readily attacked, and before use were heated some hours with hydrochloric acid. They were then washed and boiled with distilled water, and dried. Before being placed in the thermostat they were closed with rubber stoppers having a capillary tube through the per-

* From the *Journal of the American Chemical Society*, vol. xviii., No. 2, February, 1896

formation. The upper end of this extended above the water in the thermostat. The capillary opening was sufficiently fine to prevent any appreciable evaporation of the syrup while being heated. The water in the thermostat was kept at about 77.5°. Phials were removed from time to time and cooled quickly, so that the contents could be examined in the polarimeter. The following results were found:—

Time of heating in minutes.	Observed rotation.
0	32.41°
30	28.00°
60	26.25°
90	26.15°
210	24.61°
390	18.48°
570	16.60°
810	4.70°

These figures show a rapid, but an irregular, change in the rotation with the time, but as the temperature was not maintained with great accuracy, and as some of the phials were more exposed to the light than others, greater uniformity could not be expected.

To determine whether or not the inversion proceeds according to the law of Wilhelmy, a second series of experiments was made, in which the temperature was carefully regulated, and in which the small phials holding the sugar solutions were wrapped in tin-foil for protection against the light. The temperature in the last series of experiments was too low to permit them to be completed in a reasonable time. It was therefore brought to 37.5 for the following tests:—

The amounts of sugar and ferrous iodide were the same as before, but greater care was taken in the preparation of the solution. Several samples of high grade commercial sugar were tested, and one was selected which satisfied all requirements as to purity. For 250 c.c. of solution 125 grms. of this sugar are dissolved in a small quantity of water in a graduated flask by aid of heat. Then 20.5 grms. of the pure iodine, sublimed with potassium iodide, are weighed out and mixed in a flask with 50 c.c. of water and 7 grms. of pure fine iron wire. The action of the iodine on the iron begins soon, and must be checked after a time by dipping the flask in cold water. Finally, when the action is practically complete, as shown by the disappearance of the iodine and change of colour to greenish brown, the solution is boiled to make the reduction to the ferrous condition perfect. The amount of iron taken is largely in excess of that which can combine with the iodine. The ferrous solution is now allowed to cool to 50° to 60° C., and filtered into the cooled sugar solution made as above. The last traces of iodide from the flask and paper are washed down into the syrup by aid of a little boiled and cooled water. Finally, the whole volume is made up to 250 c.c. by the addition of distilled water. In this manner a solution is secured which contains, in 100 c.c., 50 grms. of saccharose and 10 grms. of ferrous iodide, and which is practically free from inversion. The specific rotation of the strong pure syrup is 66.5°; that prepared with the iodide is 64.82°, as found from the mean of many closely agreeing determinations. It will be noted that this lower specific rotation is about the same as that found for the solutions of the other salts described above. The decrease in the rotation is apparently not a result of inversion.

The method of preparation of the syrup of ferrous iodide as described in the *Pharmacopœia* leaves a product slightly inverted, because of the higher temperature of mixing the sugar and iodide solutions. When portions of the syrup made as just described are heated in boiling water an hour, in flasks with capillary stoppers to prevent evaporation, the rotation is reduced to -11.5° at 20° for the 100 m.m. tube. This value is almost identical with that calculated from the experiments of Gubbe (*Ber. d. Chem. Ges.*, 1885, 2207), viz., -11.31° for the rotation produced

by the inversion of 50 grms. of cane-sugar in 100 c.c. The presence of the excess of iodide seems to be without much influence on the specific rotation of the invert sugar.

In the experiments given below, the rotations were found in a 100 m.m. tube at 20°. The reading before heating was 32.41°, and this is taken as the initial rotation instead of the theoretical 33.25°. Applying the Wilhelmy-Ostwald formula we have—

$$\text{Nat. log. } \frac{A}{A-x} = Ct,$$

in which A represents the total amount of sugar present and may be measured by the total change in the rotation. It is therefore 32.41° - (-11.5°) = 43.91°. x represents the amount of sugar inverted at the time, t , and is measured by the decrease in rotation at that time. $A-x$ represents the sugar remaining, and the velocity of the inversion should be proportional to this. The table below gives the results of a series of experiments. The solutions were warmed two minutes before the counting of the times, t , began, as this was found necessary to bring them to the proper temperature. This, of course, introduces a small error into the calculation. The values in the fourth column are obtained by the use of common logarithms.

t min.	Observed rotation.	x	$\log \frac{A}{A-x}$	$\frac{1}{t} \log \frac{A}{A-x}$
30	28.50°	3.91°	0.04050	0.00135
60	24.85°	7.56°	0.08206	0.00137
120	17.80°	14.61°	0.17569	0.00146
180	13.35°	19.06°	0.24723	0.00137
240	6.32°	26.09°	0.39165	0.00163
300	4.32°	28.09°	0.44335	0.00148
420	-9.00°	41.41°	1.24461	0.00296

The results of the last column are sufficient to indicate that the inversion follows the general law shown by Wilhelmy to hold for the action of weak acids on sugar solutions. The values of—

$$\frac{1}{t} \log \frac{A}{A-x}$$

are not constant, but, considering the conditions of the experiment, must be considered close enough until the last one is reached. The solution of the sugar is a very strong one, containing 50 grms. in 120 c.c., and from such a degree of concentration no great regularity can be expected. The variation in the amount of water present, as the saccharose becomes changed into dextrose and levulose, must have some influence on the progress of the reaction, and one of the fundamental conditions of the Wilhelmy experiment is therefore not accurately observed. It has frequently been pointed out that the constant—

$$\frac{1}{t} \log \frac{A}{A-x}$$

may be quite irregular when calculated from tests on very strong solutions. The values are really constant only when the solvent is so greatly in excess that slight changes in it, in the progress of the reaction, may be neglected. In the present case about 2.5% grms. of water disappear in the formation of the new molecules, and this from a solution already very strong. Part of the irregularity in the constant may doubtless be explained in this manner. An accidental exposure to light during the last interval of the heating may partly account for the change in the last value.

It has been found by later experiments, some of which are still in progress, that with dilution of the solutions much more uniform results may be secured, approaching, in fact, those obtained from the action of weak acids alone.

The cause of the inversion of strong sugar solutions by these heavy salts is undoubtedly to be found in their condition of partial hydrolysis by the solvent. The acid ion in each case is a strong one, while the basic ions are all

relatively weak. Indeed, it has been suggested by Walker and Aston that the amount of hydrolysis in solutions of certain salts may be approximately measured by comparing the speed of inversion with that of known amounts of weak acids. The method can be easily applied to a large number of solutions of moderate concentration. Further investigations with special reference to ferrous salts are now in progress.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 11, March 16, 1896.

New Zirconium Carbide.—H. Moissan and M. Lengfeld.—Pure zirconia and carbon if heated in the electric furnace outside of the arc produce a carbide of the composition CZr , well crystalline and not decomposable by water at any temperature from 0° to 100° . This fact is very curious, because zirconium, which in the classification of Mendeleeff approximates to thorium, differs from it in some respects, since its carbide is very stable, whilst thorium carbide decomposes cold water with the formation of acetylene, ethylene, methane, and hydrogen. The colour of this zirconium carbide is grey with a metallic aspect. It is not affected by air, whether dry or moist, even at 100° . It scratches glass and quartz with ease, but it has no action upon ruby. The hydracids attack this carbide readily; hydrofluoric acid in the cold, hydrochloric at 250° , hydrobromic at 300° , and hydriodic at 400° . At a dull redness it burns in oxygen with much lustre. If kept in the liquid state in the electric furnace it dissolves carbon, which, on cooling, it deposits in the state of graphite. Water and ammonia have no action upon this chloride, either at the ordinary temperature or at dull redness. Concentrated nitric acid attacks zirconium carbide with violence. Oxidising agents, such as potassium nitrate, permanganate, and chlorate, attack it with energy; the action of the chlorate is explosive. Potassium has no action at its melting-point, but melted potassa dissolves it with ease.

The University of Glasgow invites the Academy to be represented at the fiftieth anniversary of the professorship of Lord Kelvin.

Principle of an Accumulator of Light.—Charles Henry.—It would be easy at present to devise an arrangement permitting us to store up solar light, and to give it out again in the night at any time desired. But an accumulator of light based upon cold would have no chance of becoming practical except in the polar regions.

Structure and Composition of the Alloys of Copper and Zinc.—Georges Charpy.—(See p. 168).

Part played by Alumina in the Composition of Glass.—Léon Appert.—The introduction of alumina into glasses prevents, or at least retards, denitrification produced by slow and repeated reductions of temperature. The presence of alumina in a glass enables us to substitute without inconvenience, and even with advantage, for a part of the alkaline base its equivalent of lime. The use of alumina may be extended to window-glass and to drinking-glasses. It may be best introduced in the state of felspar.

Journal für Praktische Chemie,
New Series, Vol. li., Part 15.

Researches from the Chemical Institute of the University of Kiel.—These consist of an investigation, by Th. Curtius and A. Blumer, on the action of hydrazin hydrate upon benzoin and desoxybenzoin.

On Dimolecular Nitriles and their Derivatives.—Ernst von Meyer.—This extensive treatise consists of a collection of facts which do not admit of abridgment.

MISCELLANEOUS.

Professor Wyndham R. Dunstan, F.R.S., has been appointed Director of the Scientific Department of the Imperial Institute, which has hitherto been under the temporary direction of Sir Frederick Abel. The principal work of this department is to investigate new or little known products from India and the Colonies, and to advise in reference to their commercial utilisation. Already much valuable work has been accomplished in this direction. With the aid of an increased grant from the Royal Commissioners of the 1851 Exhibition, further additions to the staff of this department will be made, and the laboratory, which was fitted up in 1894, with the assistance of a grant from the Goldsmiths' Company, will be considerably extended.

Royal Institution.—On Tuesday next (April 14th) Professor James Sully will begin a course of three lectures on "Child-study and Education"; on Thursday (April 16) Professor Dewar will begin a course of three lectures on "Recent Chemical Progress"; and on Saturday (April 18) Professor W. B. Richmond, R.A., will begin a course of three lectures on "The Vault of the Sistine Chapel." The Friday Evening Meetings will be resumed on April 17th, when Professor G. Lippmann will deliver a discourse on "Colour Photography."

MEETINGS FOR THE WEEK.

- MONDAY, 13th.—Society of Arts, 8. (Cantor Lectures). "Precious Stones," by Prof. Henry A. Miers, M.A.
— Society of Chemical Industry, 8. "Estimation of Moisture in Wood Pulp," by R. W. Sindall. "A Study of Comparative Affinities in the case of certain Salts of Ammonia," by Watson Smith, F.I.C.
— Medical, 8.30.
TUESDAY, 14th.—Royal Institution, 3. "Child-Study and Education," by Prof. James Sully, M.A.
— Institute of Civil Engineers, 8.
— Medical and Chirurgical, 8.30.
— Photographic, 8.
WEDNESDAY, 15th.—Society of Arts, 8. "Early English Organ Writers," by Burnham Horner.
— Meteorological, 7.30.
— Microscopical, 8.
— Geological, 8.
THURSDAY, 16th.—Royal Institution, 3. "Recent Chemical Progress," by Prof. Dewar, F.R.S.
— Institute of Electrical Engineers, 8.
FRIDAY, 17th.—Royal Institution, 9. "Colour Photography," by M. G. Lippmann.
— Quekett Club, 8.
SATURDAY, 18th.—Royal Institution, 3. "The Vault of the Sistine Chapel," by Prof. W. B. Richmond, R.A.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1899.

ON THE POWER OF RESISTANCE OF CERTAIN LIQUIDS AND OF SOME SOLIDS TO THE PASSAGE OF THE RÖNTGEN RAYS.

By MM. BLEUNARD and LAKESSE.

In a paper communicated to the Academy in the sitting of March 2nd we have explained the experimental method to which we have had recourse in undertaking this study; we now give some of the results at which we have arrived.

To express these results we have thought it indispensable to give to them coefficients which we call coefficients of penetration or of translucency; but we hitherto only employ this notation by way of simple indications or points of comparison, reserving to give a photometric method which will permit us to appreciate with precision the power of the resistance to penetration of substances by the Röntgen rays.

Our scale of coefficients increases with the transparency of the liquids, *i.e.*, that in one and the same experiment we give to the liquid which allows itself to be most easily traversed the coefficient 10, whilst complete opacity answers to 0.

We indicate below the results at which we have arrived by multiplying the experiments, and by varying on the sensitive plates the disposition of the liquids, so as to escape every error which may spring either from the intensity or the direction of the Röntgen rays, or from the sensitive plates themselves. The results given have always agreed.

I. Influence of the Degrees of Concentration.—We have exposed to Röntgen rays solutions of alkaline chlorides, bromides, and iodides, of various strengths. Sodium bromide may serve as a type.

Solution of sodium bromide at	5 per cent	10
"	10	6
"	15	3
"	20	2

As will be seen, there is no proportionality; it tends rapidly towards a limit, which is the saturation of the liquid.

II. Influence of the Non-metal.—Family of fluorine, chlorine, bromine, and iodine. Solutions of the same concentration.

Results.	Sodium fluoride	..	..	10
"	"	chloride	..	8
"	"	bromide	..	6
"	"	iodide	..	5

The Röntgen rays have so much the greater difficulty in acting upon the plates through the solutions, as the atomic weights of the non-metals are higher.

III. Influence of the Metal.—Family of lithium, sodium, potassium, and ammonium. Solutions all of the strength of 20 per cent.

		Coefficients.
Results A.—	Lithium bromide ..	10
"	Sodium bromide ..	8
"	Potassium bromide ..	3
"	Ammonium bromide ..	3
"	B.—Sodium iodide ..	10
"	Potassium iodide ..	4

The opacity increases therefore with the atomic weight of the metal; ammonium seems to form an exception, as its opacity is sensibly equal to that of potassium.

We have studied the influence of the metal in certain other absolutely different saline solutions.

Water coefficient	..	..	..	10
A.—Sodium sulphate	..	..	..	9
Copper sulphate	..	..	..	5
B.—Sodium nitrate	..	..	..	8
Potassium nitrate	..	..	..	7
Uranium nitrate	..	..	..	1
C.—Zinc chloride	..	..	..	4
Iron chloride	..	..	..	5
Manganese chloride	..	..	..	5

As in the case of the alkaline metals, the opacity of these different solutions has always increased with the atomic weight of the metal. Uranium nitrate, in particular, opposes a great resistance to the passage of the rays.

IV. Study of certain Solids.—The results obtained are still very incomplete. We intend pursuing these studies, still we are already able to give the following results:—

Family of carbon, silicon, and boron: carbon is transparent, and communicates its property to organic compounds; graphite and lamp-black are transparent for the Röntgen rays. It is the same with naphthalene, anthracene, and all the following bodies:—Gelatin, camphor, picric acid, fluoresceine, celluloid, fatty matters, alcohol, petroleum glycerin. Silicon is transparent, and seems to communicate its transparency to amorphous silica and asbestos. Boron is moderately transparent.

Family of sulphur, selenium, tellurium: opaque, with the exception of sulphur, which is slightly transmissive. Family of phosphorus and arsenic: opaque.

The results of our experiments on the greater or less resistance to the X rays, of the different solids which we have submitted to experiment agree exactly with the results obtained by Maurice Meslans, which formed the subject of a memoir submitted to the Academy on February 10th, 1896.

In fine, the opacity of substances seems to increase with the atomic weights (for saline solutions) of the metal and the non-metal.

Application.—One of us, M. Bleunard, has had the idea of applying the opacity of the alkaline bromides to the photography of characters written with an ink containing potassium bromide. A letter written with such ink, and placed in an envelope, has been completely and legibly reproduced on the sensitive plate.

We intend continuing these researches, extending them also to gases, researches which hitherto have been merely sketched.—*Comptes Rendus*, cxxii., p. 723.

ON A MEANS OF COMMUNICATING TO THE RÖNTGEN RAYS THE PROPERTY OF BEING DEFLECTED BY MAGNETS.

By A. LEFAY.

HAVING undertaken some researches on the Röntgen rays, I thought it might be useful to examine if there was not produced a change in their nature parallel to the phenomenon of the discharge of electrified bodies induced by these rays. Considerations founded on certain analogies have led me to suppose that if such a fact is exact, the modified rays ought to be sensitive to the action of a magnetic field. Under this idea I undertook, on March 4th, the following experiment:—

Below a Crookes tube, and at about $\frac{1}{4}$ c.m. from the most brilliant part, I placed a screen of lead perforated by an aperture of 2 m.m. in width; at 0.04 metre lower, a second screen of lead, having a slit of 5 m.m. in width, completely closed by a leaf of silver excessively thin, supported by a platinum wire of 1.5 m.m. in diameter,

placed exactly in the axis of the opening and opposite the silver leaf.

As it is seen, this arrangement allows us to project upon a sensitive plate placed below the shadow of a platinum wire, by the aid of a sheaf of rays determined by the two slits.

In order to modify these rays I connect the leaf of silver to the negative pole of the induction-coil, which actuates the tube so that the sheaf which traverses it has necessarily undergone the action of electrification.

The electrified rays pass then between the armatures of an electro-magnet capable of producing a field of about 400 C.G.S. units, the lines of force of which are parallel to the slits; they then meet the sensitive plate, duly surrounded with black paper, and fixed on an invariable support.

In order to show the existence of a deviation, even if very feeble, I place, during the first half of the experiment, on the right part of the sensitive plate, a screen of lead, which I cause to slide over the left part at the moment when the direction of the current in the electro-magnet changes. In this manner the reciprocal distance of the two segments of the shadow thrown by the wire gives the measure of the double deviation produced by the magnetic field.

In a first experiment, placing the sensitive plate at only 8 cm. from the armatures of the electro-magnet, I obtained a proof on which I could observe a deviation almost imperceptible, and up to a certain point capable of being attributed to an optical illusion.

It is no longer the same if we carry the plate to the distance of 15 cm.; we then obtain a proof like that which we have the honour of submitting to the Academy, and which leaves no doubt as to the exactitude of my hypothesis.

As to the direction of the deviation, it is determined by the same rule as that of the magnetic deviations of the cathodic rays in the interior of the Crookes tube.

I repeated the same experiment, under exactly the same conditions, *without electrifying the second screen*, and I obtained two shadows which prolong themselves exactly, which is conformable to the fact already known—that an electric fluid is without sensible action on the Röntgen rays.

Not having yet at my disposal other sources of electricity than the coil itself, which serves for the working of my tube, it has not been possible for me to repeat my experiments on electrifying the silver leaf by methods different from that indicated in this paper. This is a gap which I hope soon to fill up.—*Comptes Rendus*, cxxii., p. 713.

THE MECHANICAL ACTION EMANATING FROM CROOKES TUBES.

By J. R. RYDBERG.

IN No. 6 (Feb. 10, 1896) of the *Comptes Rendus*, MM. Gossart and Chevallier have shown that, in the neighbourhood of a Crookes tube, a radiometer set in motion by an extraneous heat adjusts itself before the tube with a fixed orientation after some pendulum oscillations.

The results of these offer an especial interest, because they seem to indicate an exact method of measuring the intensity of radiations if we can demonstrate that the mechanical actions observed have the same origin as the photographic action.

I have therefore repeated the experiments cited, and have obtained the same results. But on employing an ordinary electric pendulum to see if it was possible to produce these phenomena in air at the ordinary pressure, I have ascertained that all the actions observed with the radiometer derive their origin from the well-known stratum of positive electricity with which the external anti-

kathodic surface of the Crookes tube is covered during the discharges. The adjustment of the radiometer, the pendular oscillations around a position of equilibrium, the influence of the distance of the tube on the force exerted, show themselves as absolutely identical with the actions which we observed on approximating to the radiometer a conductor charged positively and of the same form as that of the tube.

As to the permeability for mechanical action, the bodies mentioned as transparent are dielectrics, whilst the opaque bodies are good conductors, which, not being insulated from the earth, have hindered the influence of the electric stratum of the tube upon the metallic wings of the radiometer.

On enclosing the radiometer in a Faraday's cylinder, formed of a thin leaf of tin, which does not arrest the photographic action, it is found that the radiation of the tube produces no more mechanical action than does—under the same conditions—a conductor charged with electricity. Under such circumstances I have been able to obtain Röntgen's photograph through a radiometer, without perceiving the least trace of mechanical action.

The persistence of the adjustment of the radiometer after the current has been interrupted, evidently derives its origin from the same source, the electric charge of the glass being lost only slowly in the ambient air. On removing in any manner the external charge of the tube, we find that the action upon the radiometer disappears instantly if the influence has not lasted long enough to induce electric strata on the sides of the radiometer.

All the modifications which, according to authors, the field of mechanical force undergoes by magnets, by electric currents, &c., are explained equally by variations of the electric fluid on the introduction of conductive bodies. A magnet only acts in this manner, no difference being perceptible between the actions of the two poles.

From all these facts we conclude that the phenomena observed by MM. Gossart and Chevallier are due to the influence of the external surface of the tube on the metallic wings of the radiometer, and have nothing to do with the Röntgen rays.—*Comptes Rendus*, cxxii., p. 715.

AN IMPROVED METHOD OF ANTHRACENE ASSAYING.

By HENRY BASSETT.

SINCE the publication of my "Note on Anthracene Testing" (*CHEMICAL NEWS*, vol. lxxi., p. 202) much of my spare time has been devoted to working out the new method therein referred to. My original object in undertaking these experiments was to find out some reliable method of discriminating between the commercial A and B qualities; as any conclusion based on the appearance of the quinones in the first stage of the usual process is (except in extreme cases) of very little value, or actually misleading, for several reasons, such as difference of percentage, and especially from differences in the character of the other hydrocarbons in the sample, and, consequently, of the products formed by their oxidation. These causes are not only sufficient to modify the appearance of the crude quinones, but also to alter their weights, as I have ascertained by experiments with pure anthraquinone, with and without the addition of known quantities of hydrocarbons and by-products.

The improved test which I now bring forward depends on the action of nitric acid, under special conditions, on the crude product of the oxidation by chromic acid. The earlier experiments in this direction were made by oxidising in the usual way, and then adding a certain quantity of nitric acid to the contents of the flask, and continuing the boiling an hour longer. Next day the dilution with water, washing with alkali, and treatment with fuming sulphuric acid were carried out as usual.

A large number of experiments made in this way gave results which, though promising, were found to be unsatisfactory in some respects, owing to the complications arising from the presence of the oxidation products in the solution, and for other reasons which would take too long to discuss in the limits of this paper.

I will now describe the method finally adopted, which has given most satisfactory results in every respect in an extended series of experiments with samples of widely different character.

The oxidation is carried out precisely in the usual manner (using 15 grms. chromic acid of about 98 per cent and free from sulphuric acid). Next morning dilute with 400 c.c. water, allow to stand for three hours, filter, and wash with cold water only; then dry the quinone on the filter in the water-oven.

Then open the filter, detach the quinone, and introduce it into a flask of the usual size, by means of a funnel with a short and wide neck, and a glass rod, using a small wash-bottle containing the conventional quantity of 45 c.c. glacial acetic acid to rinse the filter-paper, rod, and funnel. The operation is easily effected with absolutely no loss. Then add 2.5 c.c. of the chromic acid solution (= 1.5 gm. chromic acid) and 10 c.c. ordinary pure nitric acid of sp. gr. 1.42, and boil one hour with condensing tube.

Next morning dilute with 400 c.c. water, allow to stand three hours, filter, wash first with water, then with boiling 1 per cent alkali, and finally with hot water as usual. The quinone is then washed into a flat dish, dried at 100°, mixed with ten times its weight of pure concentrated sulphuric acid (not the fuming acid), and heated for ten minutes on the water-bath. It is then left all night, to absorb moisture, in a tray of water covered by a glass plate, diluted, filtered, and washed with water, boiling alkali, and hot water, exactly as in the ordinary way, and finally dried and weighed, &c.

There are several points worth noting as to the above; the first being that the presence of a small quantity of chromic acid is essential. Experiments with nitric acid alone always showed the presence of small quantities of impurities which rendered the filtration slow and unsatisfactory, and the final product retained the usual brownish colour. Only a small part of this chromic acid is reduced, although the solution becomes green. A second important point is that no difference in the results is caused by slight variations in the quantity of nitric acid used, or in the time of boiling. Of this I have satisfied myself by repeated experiments.

The effect of the treatment is indicated by the reduction in the weight of the first product as compared with a companion experiment by the ordinary test, and also in a striking manner by the colour produced on the addition of fuming sulphuric acid, which is a more or less dark brown with the ordinary test (except in the case of pure or nearly pure anthracene), while by the new method it is a clear orange colour, becoming lighter on heating—in fact, the quinone is so far purified by the preliminary treatment that the use of fuming sulphuric acid is absolutely unnecessary, as I have proved to my own complete satisfaction by a large number of comparative experiments giving identical final weights in both cases; the only difference being that the product when using the ordinary concentrated sulphuric acid is better crystallised. Lastly, with the ordinary test the colour of the final product, especially with B qualities, is more or less brownish; but with the new test it is with all samples, good or bad, a beautiful clean yellow colour, and on sublimation shows very much less carbonisation.

I must not omit to mention that a very careful examination of the final product, both by ignition with sodium and subsequent treatment with iron salts, &c., and also by heating with solution of sulphide of sodium (an exceedingly delicate test) has shown it to be perfectly free from nitro-compounds.

The following table gives the results obtained with

a fairly representative number of commercial and other samples of anthracene:—

	Ordinary test.	New test.	Loss in units.	Percent. loss on value by ord. test.
1. Commercial sample B	34.92	33.26	1.66	4.7
2. " B	32.78	31.20	1.58	4.8
3. " A	19.60	19.35	0.25	1.3
4. " A	51.19	50.68	0.51	1.0
5. " B	39.29	38.65	0.64	1.6
6. Residual product ..	18.28	16.31	1.97	10.8
7. " ..	9.24	7.06	2.18	23.6
8. Regained anthracene.	12.41	11.60	0.81	6.5
9. Experimental product	43.74	42.50	1.24	2.8
10. Commercial sample A	13.87	13.57	0.30	2.2
11. " B	35.82	34.63	1.19	3.3
12. " A	32.23	31.84	0.39	1.2
13. " Pure " anthracene..	95.27	95.02	0.25	0.26
14. Washed sample ..	61.76	61.72	0.04	0.06
15. " ..	81.75	81.15	0.60	0.73
16. Commercial sample A	82.00	81.75	0.25	0.30
17. " B	36.38	35.78	0.60	1.6
18. " B	31.37	30.52	0.85	2.7
19. " A	32.31	31.42	0.89	2.7
20. " A	41.64	40.83	0.81	1.9

The letters A and B opposite the commercial samples in the above list represent the quality usually ascribed to them in the trade. It will be seen that two of the A samples, Nos. 10 and 19, show a loss of *over* 2 per cent on the value by the ordinary test; and that two of the B samples, Nos. 5 and 17, show a loss of *under* 2 per cent. I am inclined to think that these are instances where a comparison of the results obtained by the two methods may lead to a reliable conclusion as to the quality; and also that this particular percentage loss might fairly be taken as a sort of boundary line.

The new method necessarily takes a day longer than the usual test; but I venture to think that experience will prove it to have distinct advantages in the valuation of commercial anthracenes; and I may point out, in conclusion, that it is also well adapted for the testing of crude anthraquinones.

36A, St. Andrew's Hill, E.C.

ON THE PRODUCTION OF STEEL FOR STEEL CASTINGS IN SMALL BESSEMER CONVERTERS.

By SERGIUS KERN, M.E., St. Petersburg.

NOWADAYS several systems of working small Bessemer converters have been introduced; for instance, Robert, Walrand, Tropinas.

In the CHEMICAL NEWS (vol. lxxiii., p. 111) we gave a short description of the Walrand system as worked at the Franco-Russian Works, St. Petersburg.

As several difficulties may arise elsewhere, we think it needful to make the following remarks:—

1. In calculating the charges, it is preferable to have a final product (castings) of the following average composition:—

Carbon.. ..	0.25—0.30 per cent
Silicon	0.25 "
Manganese ..	0.75 "

The joint percentage of phosphorus and sulphur must not exceed 0.08 per cent. In my process I prefer also to have in the steel 0.10 to 0.15 per cent of chromium, which is introduced with the initial charges in the form of chrome-ironstone, mixed with a ¼ per cent of lime. Such a mixture is placed with the charges made for the cupola, in the case of small Bessemer process, or, with the

charges prepared for the crucibles, in the crucible-steel process. The chief constituent of the latter charges is soft Siemens-Martin steel (scrap) of clean composition (for instance, boiler-plate scrap, coming from hole punching). My process of chromium crucible cast steel was proposed in 1878 (*Proceedings of the Iron and Steel Institute*, 1878, vol. i., p. 231). Now I find that the addition of clean raw chrome-ironstone ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) in the form of small pieces, in the quantity of one pound to every eighty pounds of the charge, makes a great improvement in the tenacity of steel castings.

2. All steel castings to be annealed in furnaces; small dimensions in layers of charcoal, and, better, in furnaces used for copper crucible melting. In such furnaces, an iron plate is placed on the fire-bars; next is placed a layer, 6 inches thick, of charcoal, then about 5 cwt. of small steel castings, which are covered with a layer of charcoal 6 inches thick. The lid of the furnace is closed, and the seams are lined with clay. After thirty hours the articles are drawn out, and the operation repeated a second time.

3. We recommend the use for the bottom of the converters good fire-bricks of pyramidal sections, about 10 to 12 inches high; one brick for each tuyere. The lining of the sides is made of a neutral material; lump of chrome-ironstone cemented with a mixture of powdered mineral with lime (3 parts to one part).

4. After the over-blow, the slag is drawn out by means of iron bars inserted into the converter, and fluid silico-spiegel is added (about 5 per cent, containing 10 per cent of silicon and 20 per cent of manganese). Sometimes it is suitable to add also a $\frac{1}{2}$ per cent of 80 per cent ferro-manganese. All this being added, the metal is quietly mixed by iron bars; the converter remaining all this time in a horizontal position, and *no—even quite short—over-blow is made*. Such over-blows for mixing the additions only spoil the quietness of the metal—what inventors, it seems, do not understand, as they often produce over-blows at this part of the process, which certainly spoil the metal, giving rising steel.

5. In order to avoid the last-mentioned nuisance, the ladles must be red-hot before pouring steel into them, and about 0.1 per cent of aluminium must be thrown into them.

We must conclude our short note by saying again that chrome-ironstone has a marvellous effect on steel, when properly applied. As a paint for steel mouldings, we used for several months Stephen's silica moulders' paint, and with good effect, too.

INCREASE IN TEMPERATURE OF CELLULOSE ON ABSORPTION OF ATMOSPHERIC MOISTURE.

By CLAYTON BEADLE and O. W. DAHL.

ONE of us observed that anhydrous cellulose rose in temperature whilst taking up moisture from the atmosphere, and that this rise of temperature appeared to have some relation to the increase in weight (*Nature*, xlix., 457; and *CHEMICAL NEWS*, lxxi., 1).

The above experiments were done with cotton-wool alone. We have carefully repeated these experiments, but using, in addition to cotton-wool (whose fibres were 20–30 m.m. in length), cotton mechanically disintegrated by a dry process (fibres reduced to 1–1.5 m.m.), and a finely-powdered amorphous form of cellulose, which we shall refer to as "viscoid." Viscoid is obtained by treating cotton with strong alkali and carbon disulphide, dissolving the cellulose thiocarbonate obtained in water, and regenerating the cellulose as a gelatinous mass by heat. The mass is broken up, washed free from by-products, dried down, and ground to powder.

In all cases the moisture was removed from the samples

by placing them in a water-bath. In the case of the cotton-wool the percentage is reckoned, and the weight taken before placing in water-bath. In the cases of the disintegrated cotton and pulverised viscoid, the weight at which the samples remain constant is reckoned at 100, and the other weights calculated on this.

It will be noticed by examining the curves for the cotton-wool (Fig. 1) that the two curves run fairly closely, except in the centres, where they diverge considerably. This difference we are unable to explain. It will be noticed, also, that the final weights are short of the air-dry weights by about 0.75 per cent. This appears to be due to the loss of something other than water when the fibre was heated. The disintegrated cotton, which is chemically identical with the cotton-wool, gains much less before it comes to a constant weight. The curves in this instance are much more regular, the disintegrated cotton resembles the cotton-wool in that it becomes constant in weight in about the same period of time, viz., about one hour.

In the case of the powdered viscoid (Fig. 2), the fine gives the most regular curve, but starts from a higher point than the coarse. These two were tried with a view of seeing whether the coarseness of the grain would affect the curve.

Table I. is a summary of the various determinations of the increase in weight. The weighings were in each case done in a weighing tube, and the material removed from the tube and spread out on a tray for exposure.

The three sets of curves in Figs. 1 and 2 resemble each other somewhat closely, and we are inclined to think that the physical condition or structure of the cellulose does not materially affect the character of the curve.

One thing is apparent from these experiments, and that is that the percentage of moisture taken up decreases with the fineness of the cellulose. This is true with cellulose in the fibrous form, such as cotton, as well as with viscoids. The fact that large masses of viscoid have a much higher hygroscopic moisture than viscoid after pulverising lends support to this view. It is also noticeable that, *ceteris paribus*, the curve becomes more uniform with the fineness of the particles of the cellulose. Thus, we notice that the cotton-wool curves are somewhat irregular, but that the same after disintegration are more regular. The coarse powdered viscoid is also much less regular than the fine powdered.

In order to determine the rise in temperature, the cellulose in each, after drying in the water-bath and allowing to cool to the temperature of the atmosphere in a weighing tube, was placed round the bulb of a sensitive thermometer; and a similar thermometer placed at a distance of about four inches was used to indicate the temperature of the atmosphere. The cotton-wool was merely tied on to the bulb of the thermometer, but the pulverised cotton and viscoid were contained in a cage of thin wire gauze, so as to allow free access of the air. The readings are contained in Table II. The curves in Figs. 3 and 4 represent temperature of the cellulose when the temperature of the atmosphere is reduced to a straight line. The two lower curves in Fig. 3 are given by cotton-wool. The lower curve was distorted somewhat by the fact that the temperature of the air did not remain constant. Certain close resemblances between the two curves for cotton-wool can, however, be noticed. The curves for the disintegrated cotton are much more regular and run much closer. Here, again, we see that the fineness tends to regularity. There is, however, an important difference between disintegrated cotton 1 and 2: 1 rises from the beginning, but 2 gives a dip below the atmospheric temperature during the first two seconds. It will be noticed that cotton-wool reaches the temperature of the surrounding air about the time that the weights become constant; whereas the disintegrated cotton is still more than 4° above.

The curves with the powdered viscoid show in each case a rapid fall in temperature during the first minute.

FIG. 1.—Increase in Weight of Dry Cotton by Exposure to the Air.

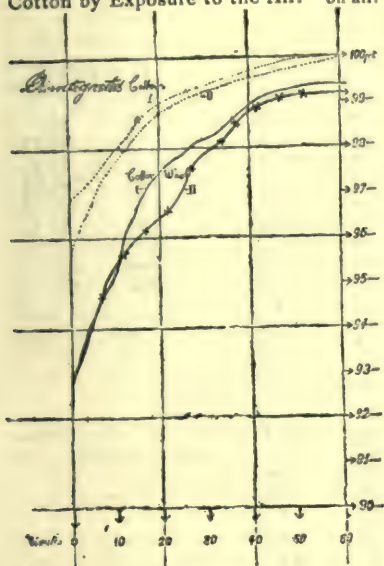


FIG. 2.—Increase in Weight of Dry Viscoid Powdered by Exposure to the Air.

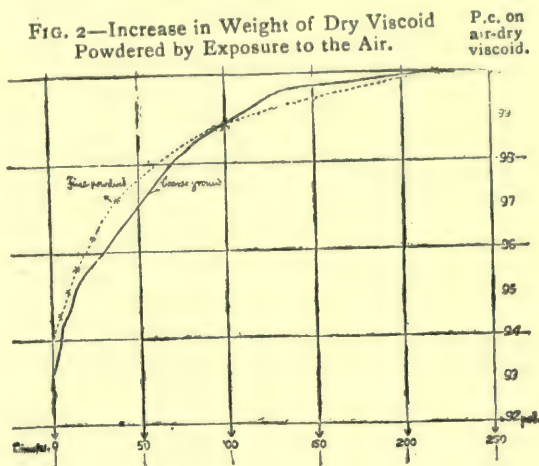


FIG. 3.—Temperature Curves.

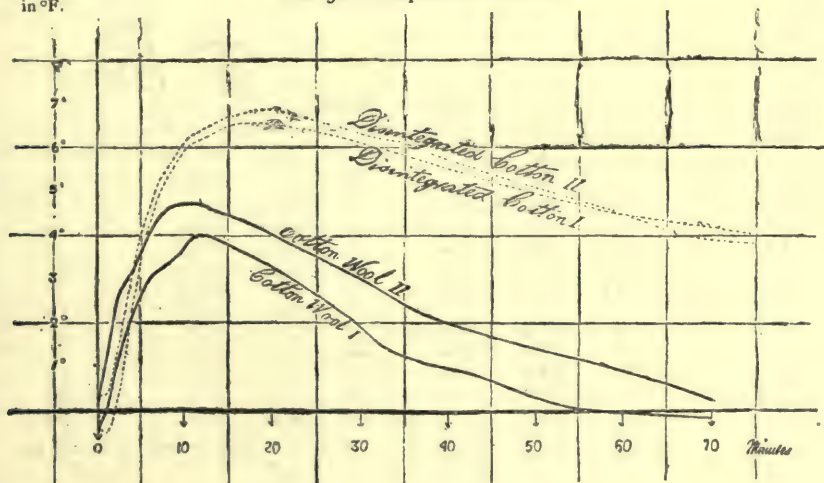


FIG. 4.—Temperature Curves.

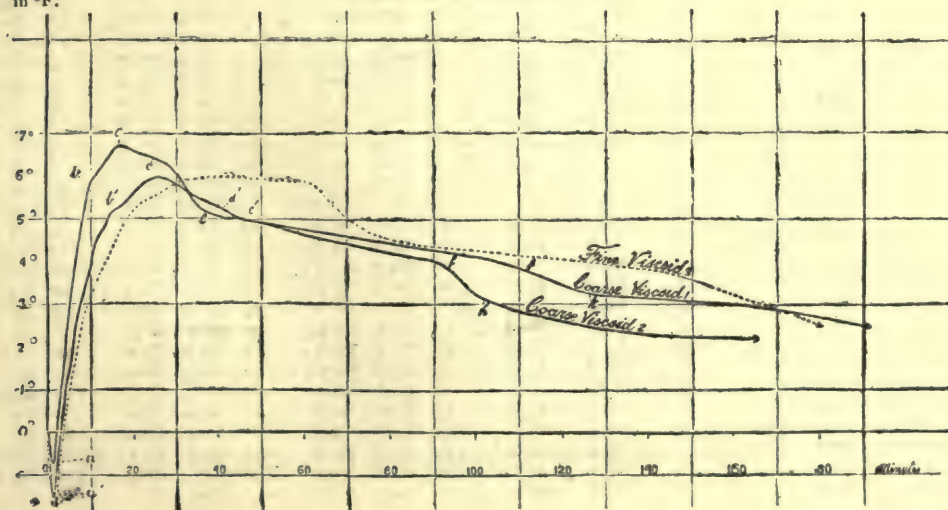


TABLE I.—Increase in Weight by Exposure to the Air of—

COTTON-WOOL.			DISINTEGRATED COTTON.			Coarse Powdered.			Fine Powdered.		
I.			II.*			I.					
Min.	P.c.		Min.	P.c.		Min.	P.c.		Min.	P.c.	
0	92'7		0	92'85		0	93'2		0	94'0	
1	93'1		1	93'10		1	93'3		5	94'55	
2	93'5		2	93'3		2	93'4		10	95'1	
3	93'7		3	93'7		3	93'65		15	95'65	
4	94'05		4	93'9		4	93'75		25	96'35	
5	94'25		5	94'2		5	93'90		37	97'2	
6	94'5		6	94'55		6	94'25		100	98'9	
7	94'75		7	94'75		7	94'40		220	100	
8	94'9		8	95'00		8	94'45		230	100	
9	95'05		10	95'35		9	94'5				
10	95'25		12	95'65		10	94'6				
12	96'05		17	96'20		11	94'75				
13	96'30		22	96'60		12	94'85				
14	96'40		27	97'55		13	95'0				
15	96'7		32	98'15		14	95'15				
18	97'25		37	98'55		15	95'20				
20	97'45		42	98'90		20	95'55				
22	97'70		47	99'05		30	96'00				
24	97'80		52	99'15		40	96'50				
25	97'90		62	99'15		50	97'05				
29	98'15					70	98'05				
31	98'20					80	98'35				
36	98'60					90	98'65				
41	99'00					100	98'90				
46	99'20					115	99'25				
51	99'30					145	99'70				
55	99'35					200	99'95				
60	99'35					220	100'00				

* For this series see CHEM. NEWS, vol. lxxi, p. 1.

TABLE II.—Temperature.

DISINTEGRATED COTTON (exp. to the Air).					
I.			II.		
Min.	Air.	Cell.	Min.	Air.	Cell.
0	63'8	63'8	0	53'9	54'2
1	64'0	63'4	1	53'9	54'2
2	64'1	64'1	2	54'0	55'0
3	64'1	65'1	3½	54'0	56'5
4	64'3	66'6	5	53'9	57'9
5	64'3	67'8	6	53'9	58'5
6	64'4	68'6	8	53'9	59'4
7	64'5	69'4	10	53'9	60'0
8	64'7	70'0	12	54'0	60'4
9	64'9	70'5	14	54'0	60'6
10	65'0	70'9	18	54'0	60'8
11	65'0	71'1	20	54'0	60'9
13	65'1	71'4	25	54'0	60'6
15	65'4	71'9	30	53'9	60'2
20	65'6	72'1	35	53'9	60'0
30	66'0	72'1	40	53'8	59'5
40	66'5	72'0	45	53'6	59'0
60	66'5	71'0	50	53'9	59'0
120	64'0	66'0	60	54'1	58'6
180	66'6	66'7	75	54'2	58'0
			90	54'0	57'0
			105	54'0	56'5

COTTON-WOOL (Exposure to the Air).					
I.			II.		
Min.	Air.	Cell.	Min.	Air.	Cell.
0	55'6	55'1° F.	0	61'8	62'0
1	56'0	56'0	1	62'4	63'4
2	56'1	56'9	2	62'6	64'8
3	56'2	57'7	3	62'7	65'5
4	56'3	58'4	4	62'9	66'0
5	56'4	59'0	5	63'0	66'6
6	56'5	59'5	6	63'0	67'0
7	56'7	59'9	7	63'0	67'4
8	56'8	60'1	8	63'2	67'8
9	56'9	60'4	9	63'3	68'0
10	57'0	60'7	10	63'4	68'1
11	57'0	61'0	11	63'5	68'2
12	57'0	61'0	12	63'6	68'3

COTTON-WOOL (Exposure to the Air). (Continued).

I.			II.			III.		
Min.	Air.	Cell.	Min.	Air.	Cell.	Min.	Air.	Cell.
13	57'1	61'1	13	63'8	68'4	0	63'8	63'6
18	57'5	61'0	15	63'9	68'4	1	64'0	62'3
23	58'0	60'9	20	63'8	67'9	2	64'0	63'1
28	58'2	60'4	25	63'8	67'4	3	64'1	63'8
33	58'9	60'3	30	63'7	66'7	4	64'1	64'3
38	59'0	60'0	35	63'7	66'1	5	64'2	65'0
43	59'2	60'0	40	63'6	65'6	6	64'2	65'5
48	59'6	60'0	45	63'5	65'1	7	64'3	66'1
53	59'9	60'0	50	63'4	64'8	8	64'4	66'8
58	60'0	60'0	60	63'4	64'3	10	64'7	67'8
70	60'6	60'4	70	63'4	63'7	12	64'8	68'5

Viscoid (Exposure to the Air).								
I.			II.			III.		
Min.	Air.	Cell.	Min.	Air.	Cell.	Min.	Air.	Cell.
0	61'8	61'0	0	62'0	62'0	0	63'8	63'6
1	62'0	60'5	1	62'0	61'3	1	64'0	62'3
2	62'0	61'0	2	62'0	62'0	2	64'0	63'1
3	62'0	62'0	3	62'0	62'7	3	64'1	63'8
4	62'0	62'8	4	62'0	63'9	4	64'1	64'3
5	62'1	63'6	5	62'1	65'0	5	64'2	65'0
6	62'2	64'2	6	62'1	65'6	6	64'2	65'5
7	62'3	65'0	8	62'1	66'9	7	64'3	66'1
8	62'4	65'5	10	62'0	67'8	8	64'4	66'8
9	62'5	66'0	12	62'0	68'1	10	64'7	67'8
10	62'5	66'5	15	62'0	68'6	12	64'8	68'5
11	62'5	66'9	17	62'0	68'7	13	64'9	68'8
12	62'5	67'1	20	62'0	68'7	15	64'9	69'2
13	62'6	67'4	21	62'0	68'6	20	64'9	70'1
14	62'7	67'7	22	62'0	68'5	30	65'2	71'0
15	62'8	68'0	25	62'0	68'4	40	65'0	71'0
17	62'9	68'15	30	62'0	68'1	60	64'0	69'8
20	63'0	68'6	35	68'0	62'7	70	64'0	69'0
25	63'0	69'0	40	62'9	68'0	80	64'5	68'9
35	63'5	69'0	50	62'7	67'6	140	62'9	66'7
45	64'0	69'0	60	62'6	67'4	180	65'0	67'5
100	62'7	66'8	90	62'4	66'4	260	67'1	69'0
160	63'0	66'0	100	63'9	67'1	300	65'0	66'9
280	62'5	63'8	130	64'0	66'4	330	65'7	67'5
340	62'5	63'8	160	64'0	66'2	360	66'0	67'4

We are entirely at a loss to account for this fall. The temperature then suddenly rises. A glance at the two curves given with the coarse viscid shows that they resemble one another very closely. Thus, the points a, b, c, d, e , &c., correspond with the points a', b', c', d', e' , &c. With the finely-ground viscid we find, again, that the curve is much more regular, and in addition to this, we see that when the maximum is reached, the temperature remains almost stationary for about fifteen minutes; whereas with the coarse viscid the temperature falls immediately after reaching the maximum. With the exception of this, the curves for the coarse and fine viscid in a large measure resemble each other. It is impossible at present to draw any conclusion from these curves as to the nature of these changes, and we must await the issue of further work for an explanation.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 173).

The Electric Spectra of Barium.—On several occasions I have instituted researches on the electric spectrum of chloride and oxide of barium, obtained by the dissociation of chloride or carbonate of barium. These researches have enabled me to enunciate the following facts:—

The colour and luminosity of a spark half a c.m. in length, made by reducing a five c.m. spark, flashing between pure platinum balls coated with fused chloride of barium, barely differed from the colour and luminosity of the same spark in pure air; whilst the same chloride, when moist, coloured the spark a slightly yellowish green. The green colour was more pronounced, with a uniform distance between the balls, when the length of the un-reduced spark was greater. The discharge from a coil with a condenser, giving sparks 15 c.m. in length, between platinum balls coated with fused chloride of barium, was very bright, and coloured greenish yellow.

The colour and luminosity of a spark charged with chloride of barium are therefore functions at the same time of the volatility of the compound and of the intensity of the electrical phenomena.

These facts are more noticeable with oxide of barium. The eye can detect no difference between the colour and luminosity of a 5 c.m. spark and those of a 15 c.m. spark under the same conditions.

On moistening the balls with a saturated solution of oxide, a very pale green colour is seen.

On the other hand, a discharge between the balls coated with the same oxide and half a c.m. apart, from a coil with a Leyden jar capable of giving 15 c.m. sparks, is coloured a strong yellowish green. The luminosity of the discharge is further increased by wetting the balls, coated with fused oxide, with an aqueous solution of the same compound.

Therefore chloride and oxide are similar in this respect, the intensity of the light they impart to a spark is a function of their relative volatility, and of the electrical power employed.

Spectrum analysis of a spark or discharge saturated with chloride or oxide confirms the above facts.

I completely covered the pure platinum balls with chloride, by plunging them several times into this compound when heated fully up to the point of igneous fusion. Without allowing them time to absorb moisture from the air, I arranged them, from 3 to 5 m.m. apart, in front of the slit of the Steinheil spectroscope. Having passed a spark by means of a coil giving 5 c.m. sparks, I detected the barium spectrum, consisting of its characteristic lines, strong at their ends and weak towards their middle, and very faintly coloured, as though the spectrum

of the ends of the spark only was seen. On removing the diaphragm, so as to expose the full height of the field of the spectrum, I became certain that from one-half to two-thirds of the length of the lines was missing, according to the distance between the coated balls.

I repeated these observations very often, and there can be no doubt as to their accuracy.

Having noted the result, without interrupting the sparks, I wetted the coated balls with a saturated solution of chloride, by means of a small platinum spoon attached to a glass tube. The spark was immediately coloured green, and, without exception, all the lines became perfect, and at the same time acquired their proper colour and luminosity.

I tried to repeat this when using the large Hilger instead of the Steinheil spectroscope. When using successively three and five Iceland spar prisms, I failed to notice the lines faded away either in their middles or at their ends; all of the few I could see were complete, but extremely faint.

I moistened the coated balls by means of a chloride solution, and immediately the luminosity of the barium spectrum increased to the same degree as that of the spark, and I saw a perfect electric spectrum of barium.

I replaced the chloride by oxide of barium newly prepared by the action of an oxyhydrogen blowpipe on chloride. When using the Steinheil spectroscope I found the same facts in a more marked degree. *The lines were still more incomplete, more evanescent towards the centre, and the colour of the parts seen was also less bright.* To perfect the lines, it was sufficient to increase the luminosity of the spark. This result was attained by wetting the dry oxide with an aqueous solution of itself, or even with pure water; but it is not possible to reproduce in this manner the colour intensity of the lines in the spectrum of dry chloride, which is more volatile than dry oxide.

These facts agree with those noted by M. Fiévez, and the explanation he gives appears to me to be incontestable. It is well known that he attributes the existence or absence of imperfect lines to the degree of luminosity.

The luminosity of the electric radiations from baryta is comparatively slight. For instance, when examining an electric barium spectrum formed by analysis of a spark from 2 to 5 m.m. long, passing between platinum balls coated with dry chloride or oxide of barium, or even wetted with a saturated solution of either of these salts, if a Bunsen burner charged with thallium, or one of its compounds, be placed behind the spark charged with baryta, so that thallium rays pass through this latter, the barium spectrum is seen to be extinguished and replaced by the thallium spectrum. By interposing a movable screen in front of the thallium flame and behind the balls coated with the baryta compound, I could, at will, cause the *appearance or disappearance* of the electric spectrum of barium, or the flame spectrum of thallium, using either the Steinheil, Duboscq, or large Hilger spectroscopes, the latter fitted with three Iceland spar prisms.

The rays emitted by the Bunsen flame charged with metallic thallium were so intense that I succeeded in completely extinguishing the barium spectrum in an electric discharge from an induction-coil capable of giving 15 c.m. sparks, but reduced to 5 m.m.

It remained to find out whether radiations from a flame or electric arc charged with thallium were capable of interfering with an arc spectrum of baryta.

Regarding the electric spectrum of barium, my repeated observations of its compounds made under varying conditions confirm Bunsen's statements about the spectrum of its chloride. I found the spectrum of oxide to be identical with that of the chloride, as regards the colour intensity of corresponding lines and the complete absence of the sodium line. I found that the spectra of an electric spark, discharge, and arc, made by means of a battery of thirty very large Bunsen cells, were formed entirely of the same extremely sharp lines. This fact is very remark-

able, and it is not observed to the same degree with the electric spectra of compounds of calcium and strontium, notwithstanding their brilliancy.

I took very great care in enumerating and determining the positions of the lines in the electric barium spectrum, by means of the Steinheil spectrocope, and in comparing my results with Bunsen's determinations, made by means of a spectrocope of the same pattern.—

	I found	Bunsen gave
	Div.	Div.
In the red ..	{ Two strong lines at	{ 36°50
		{ 44°00
	{ Two weak lines „	{ 44°50
		{ 45°80
In the yellow	{ A strong line „	{ 51°00
	{ A weak line „	{ 52°00
In the green	{ A strong line „	{ 60°40
	{ A weak line „	{ 63°00
In the bluish green ..	{ A strong line „	{ 82°00
	{ A weak line „	{ 83°00
In the blue	A strong line „	101°75
		108°50

These results agree when an allowance is made, by calculation, for the difference in the refractive power of the prisms of the two spectroscopes used.

The flame and electric spectra of barium show both common and specific lines. The bands in the flame spectrum from 35°0 to 37°0, from 43°5 to 46°0, and from 54°5 to 66°25, on the Steinheil spectrocope, corresponding to from 34°0 to 36°0, from 43°0 to 46°0, and from 61°0 to 63°0 on the Bunsen spectrocope, are represented by strong or weak lines in the electric spectrum at 36°5, 44°0, 44°5, 45°8, and 60°4 on the Steinheil spectrocope, corresponding to 35°5, 43°5, 44°0, 45°5, and 65°0 on the Bunsen spectrocope. The strong bands from 39°0 to 41°0, the bands from 54°5 to 55°25, from 56°0 to 57°0, from 63°5 to 66°0, at 67°75, at 70°75, from 72°5 to 80°0, and finally the nebulous line from 84°25 to 86°0, on the Steinheil spectrocope, corresponding to from 55°0 to 56°0, from 57°0 to 58°0, from 65°5 to 68°0, from 70°0 to 74°0, and from 89°0 to 91°0, on the Bunsen spectrocope, are not found in the electric spectrum.

The strong lines in the electric spectrum seen with the Steinheil spectrocope at 51, 82, and 101°7, corresponding to 51, 86, and 108°5 on the Bunsen spectrocope, are entirely wanting in the flame spectra. I enumerated the bands in the flame spectrum, made in oxyhydrogen gas, and also determined the position of the lines in each of the spectra, by superposing the two types as accurately as possible. These differences, which have been the subject of most minute investigation on my part, were first detected by Bunsen, and shown by him in the plates accompanying his work; I consider them to be absolutely demonstrated.

The difference between these two types of spectra is so great that, even after having produced and reproduced them from the same body, one is hardly convinced that they belong to an element: I was likewise struck with astonishment when I first compared, by a most accurate superposition, the electric with the flame spectra of the same chloride of barium, and using the same instrument.

The electric spectrum has been shown to be unchangeable; in the colour intensity of corresponding lines, the spectrum of the weakest spark saturated with dry chloride of barium is identical with the spectrum of the most powerful electric discharge or arc I have at my disposal. Every attempt I made, by raising the temperature, to change either of the flame spectra into the electric spectrum, ABSOLUTELY failed, and vice versa. Judging from my own experience, I must consider that the flame and electric spectra of barium are not convertible the one into the other.

Barium, then, in this respect resembles calcium, strontium, sodium, and lithium; the flame and electric spectra of these metals are, in fact, of different types, however much each may appear to resemble the other.

The difference noticed between the flame spectra is probably due to inequality of temperature,—at least experience tends to that conclusion. Can the difference between the complete flame spectrum and the electric spectrum be due to the same cause,—that is to say, to the inequality of the temperatures of an oxyhydrogen blowpipe and an electric spark, causing radiations of different intensities? As a matter of fact, this relative intensity can cause to appear or prevent the appearance, or at least the visibility, of certain lines.

(To be continued).

THE COMPOSITION OF WATER. A SHORT BIBLIOGRAPHY.

By T. C. WARRINGTON, B.A.

(Concluded from p. 171).

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J. C. S., (1879), xxxv., p. 232.
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Amer. Journ. Sci., (1883), [3], xxvi., p. 63.
In the course of the paper (Expt. 6) the author finds that the ratio O : H, on burning hydrogen with copper oxide, is not constant with varying conditions.
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"Das Verhalten des Wasserstoffs zu Blei und anderen Metallen."

Sitzungs. Akad. Wien., (1891), c., C, II. b, p. 618.

Monat. für Chem., (1891), xii., p. 642.

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Nature, (1892), xli., p. 151.

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"Détermination des Poids Atomiques par la Méthode Limite."

Compt. Rend., (1893), cxvi., p. 753.

The observations of Dumas on the Composition of water are used as an example.

(67). 1893. G. HINRICHS.

"Détermination du Poids Atomique Véritable de l'Hydrogène." (Note).

Compt. Rend., (1893), cxvii., p. 665.

Chem. News, (1893), lxxiii., p. 269.

The observations of several observers are reduced by the limit method (65).

Of subordinate points, the *purity of the hydrogen* used is discussed in Nos. 5, 12, 13, 18, 20, 25, 28, 30, 34, 37, 38, 39, 44, 46, 49, 50, 61;

The *purity of the oxygen* used in Nos. 5, 12, 13, 18, 20, 23, 25, 28, 30;

The *occlusion of gases by copper* in Nos. 34, 39, 43, 48, 49, 54, 63;

The *purity of copper and copper oxide* used in Nos. 35, 38, 39, 44, 47, 48, 49, 50;

The *reduction of weighings to vacuo* in Nos. 34, 35, 36, 37, 38, 39.

Criticisms of previous work will be found in Nos. 5, 9, 14, 15, 17, 18, 20, 21, 22, 25, 26, 30, 36, 37, 38, 39, 42, 44, 48, 50, 53, 56, 57, 58, 59, 60, 61, 62, 64, 65, 66, 67.

The Sixty-eighth Meeting of German Naturalists and Physicians.—This Congress will be held this year from September 21st to 26th at Frankfort-on-the-Main. The President of the Chemical Section (No. 3) is Dr. Theodor Petersen, and the Secretary Dr. Martin Freund. It is requested that papers to be read and demonstrations to be submitted may be announced to these gentlemen up to the end of May. It will be remembered that the German term "Naturforscher," which we are obliged to translate by "Naturalist," includes all persons who study any department of natural science.

NOTICES OF BOOKS.

The Medical Register. Printed and Published under the Direction of the General Council of Medical Education and Registration of the United Kingdom pursuant to an Act passed in the Year XXI. and XXII. Victoriae, Cap. XC., entitled "An Act to Regulate the Qualifications of Practitioners in Medicine and Surgery." 1896. London: Printed for the General Medical Council at Her Majesty's Printing Office, and Published and Sold for the Council by Spottiswoode and Co., 54, Gracechurch Street, E.C.

By far the greater part of this goodly volume is taken up with a catalogue of the registered practitioners in the United Kingdom, or if not resident in such kingdom, qualified to carry on their profession therein if such be their pleasure.

There are abstracts of the original Medical Act of 1858, with its amendments, technically so-called. There are laid down the rights and privileges of registered practitioners, and the disabilities of unqualified pretenders acting as physicians or surgeons. It is to be remarked that these disabilities are not so stringent as to prevent the wholesale exercise of quackery, and that under their sway the charlatan is often able to amass wealth such as the most eminent physician cannot reach. The difficulties in the way of striking out unqualified persons from the register are often serious. An important desideratum is the formation of an Imperial register for the entire dominions of Her Majesty. We may note with satisfaction as a far-off step in this direction the compilation of an Imperial Pharmacopœia.

The Dentists' Register. Printed and Published under the Direction of the General Council of Medical Education and Registration of the United Kingdom, pursuant to an Act passed in the Year XLI. and XLII. Victoriae, Cap. XXXIII. entitled "An Act to Amend the Law relating to Dental Practitioners." 1896. London: Printed for the General Medical Council at Her Majesty's Printing Office, and Published and Sold for the Council by Spottiswoode and Co., 54, Gracechurch Street, E.C.

We have here the "Dentists' Act" in full. Among the provisions here recognised as binding there are some whose necessity, or their *raison d'être*, is not very clearly apparent. Thus no medical authority is to impose upon candidates for examination an obligation to adopt, or refrain from adopting, the practice of any particular theory of dentistry or dental surgery! Surely a case so unlikely need scarcely have been specially provided against. It would appear that a very large proportion of the dentists here registered were in practice before July 22nd, 1878.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., No. 12, March 23, 1896.

Invisible Radiations emitted by the Salts of Uranium.—Henri Becquerel.—Already inserted.

Observations on M. Becquerel's Communication.—L. Troost.

Observations on a Paper by Charles Henry entitled "On the Principle of a Luminous Accumulator."—Henri Becquerel.—The author shows that the prevention of the emission of light by intense cold had been studied by Canton as far back as 1764, as well as by Becquerel, sen., and by Raoul Pictet.

Application of the X Rays for the Diagnosis of Surgical Affections.—M. Lannelongue.—Instances of the successful application of the Röntgen rays in the detection of surgical injuries.

Researches on Rare Earths contained in Monazitic Sands.—P. Schützenberger and O. Boudouard.—This paper will be inserted in full.

Quantities of Nitric Acid contained in the Waters of the Seine and its Principal Affluents.—Th. Schlösing.—The essential conclusion of the present paper is that the rivers in the entire basin of the Seine have similar phases as regards nitric acid. They present simultaneously their highest standards after a prolonged depression of the temperature has suspended the aquatic vegetation and suppressed the influx of drainage water. Consequently, it is possible to select the time and the place for taking samples of water for ascertaining its maximum standard of nitric acid.

On a Means of Imparting to Röntgen Rays the Property of being Deflected by a Magnet.—(See p. 177).

Mechanical Action emanating from Crookes Tubes.—J. R. Rydberg.—(See p. 178).

Origin of the Röntgen Rays.—Jean Perrin.—The author finds that Röntgen rays are developed at points where the cathodic rays are arrested by any substance whatever, and do not appear to develop at other parts. These rays diverge in all directions; only certain substances, such as crystals, absorb them rapidly.

Researches concerning the Properties of the X Rays.—Prince B. Galitzine and A. de Karnojitzky.—This paper will be inserted in full.

Reduction of the Time of Exposure for Röntgen Photographs.—Georges Meslin.

Procedure allowing an Abridgment of the Time of Exposure for Photography with the X Rays.—M. Basilewski.

Reduction of the Time of Exposure in Photography with the X Rays.—A. Imbert and H. Bertin-Sans.—These three papers will be summarised jointly.

On the X Rays.—M. Piltchikoff.—On employing a Puluj tube excited by a Wimshurst machine I have obtained a photographic proof in two seconds. This duration of exposure was amply sufficient, the phosphorescent plate of the tube being at the distance of 4 c.m. from the sensitive plate. The author has demonstrated the non-influence of electrostatic actions upon the X rays. He has also shown, along with other physicists, the transparency of the diamond for these rays, and their discharging action upon an electrolysed body (sodium amalgam).

Power of Resistance of certain Liquids and Solids to the Passage of the Röntgen Rays.—MM. Bleunard and Labesse.—(See p. 177).

Action of the X Rays upon Precious Stones.—Abel Buguet and Albert Gascard.—The transparency of aluminium for the X rays led us to think that its compounds might retain some of this property. Crystallised alumina, which, next to diamond, constitutes—under the names of corundum, ruby, sapphire, emerald, topaz, and cat's-eye—the majority of the most valuable stones, distinguishes the latter and its imitations from the above-mentioned stones. Turquoise (aluminium phosphate) is also thus certainly distinguished from its imitations. Natural aluminium mellate (mellite) is almost as transparent as carbon. Fine pearls of small size are less opaque than false ones of the same size, and may be clearly distinguished by the X rays. For large pearls the distinction is not certain.

Three cases of the Surgical Application of Röntgen Photographs.—Pierre Delbet.—This memoir is of great surgical interest, but does not reveal any new properties of the X rays.

The Rays of Röntgen in the Eye.—Dr. Wuillomont.—From experiments on a rabbit, the author concludes that the opacity of the eye to the X rays is not absolute. In a second series of experiments made on a human head the results were negative, notwithstanding very intense radiation and prolonged exposure.

Novel Element contained in Rare Earths bordering on those of Samarium.—Eug. Demarcay.—Already inserted.

Action of Reducing Agents upon the Compounds of Nitroso-ruthenium.—L. Baizard.—The preparation of a ruthenium nitroso-oxide by the action of ammonia upon potassium ruthenate approximates to the preparation of potassium osmiumate by the action of ammonia upon the osmate.

Amalgams of Molybdenum, and some Properties of Metallic Molybdenum.—J. Feré.—The properties of molybdenum obtained from its amalgam by distillation *in vacuo* at a low temperature are quite different from those of molybdenum as hitherto obtained. The substance is pyrophoric, ignites in the air, yielding molybdic oxides, which are partially volatilised by the heat liberated. It loses this property if heated above 400°. It becomes incandescent in a current of sulphurous acid, which is entirely absorbed, forming molybdenum sulphide and molybdic oxides. Nitrogen, carbonic acid, and hydrogen sulphide seem to have no action at the ordinary temperature or at a gentle heat. Carbon monoxide is rapidly decomposed.

Products of the Distillation of Wood. (Experiments made on an Industrial Scale).—Ernest Barillot.—The author gives his results in the form of tables.

Isomerism in the Aromatic Series.—Oechsner de Coninck.—The author has already shown that the aromatic isomers resemble each other two by two if submitted to various physical and chemical reactions. The same conclusion is reached on comparing the ebullition and fusion points of the principle aromatic derivatives.

Rhodinol and its Transformation into Menthone.—Ph. Barbier and L. Bouveault.—Not suitable for useful abstraction.

Journal für Praktische Chemie,
New Series, Vol. II., Part 15.

A Reply by F. Stolz to the Memoir of R. von Rothenburg.—The subject of the discussion is the constitution of the *n*-phenylpyrazolones. The spirit in which it is now conducted may, perhaps, be judged from the opening sentence of the paper now before us:—"In the memoir referred to, R. von Rothenburg advances no new evidence in support of his position, but merely repeats errors which have long ago been refuted, to which he appends a new one of similar value."

On Reductions by means of Phenylhydrazin.—R. Walther.—The author shows that at an elevated temperature phenylhydrazin reacts violently with azobenzene, the products being from the azobenzene, hydrazobenzene, and from phenylhydrazinbenzene with an escape of nitrogen. The author has examined further reductive actions of phenylhydrazin.

Flashing-point of Petroleum.—The *Chemiker Zeitung* of March 28th contains a most thorough-going paper on the petroleum question from the pen of Dr. O. A. Lobry de Bruyn. He pleads for an international agreement on the flashing-point of mineral oils, which should not fall below a minimum of 40° C. Referring to the recognised fact that one death weekly is traced in London alone to lamp accidents, and in the whole of Britain one daily, he asks whether a moral question of such gravity should be buried under a heap of dollars?

MEETINGS FOR THE WEEK.

- MONDAY, 20th.—Society of Arts, 8. (Cantor Lectures). "Precious Stones," by Prof. Henry A. Miers, M.A.
- TUESDAY, 21st.—Royal Institution, 3. "Child-Study and Education," by Prof. James Sully, M.A.
- Institute of Civil Engineers, 8.
- Pathological, 8.30.
- Photographic, 8.
- WEDNESDAY, 22nd.—Society of Arts, 8. "The Perfected Photo-chromosome and its Colour Photographs," by F. E. Ives.
- THURSDAY, 23rd.—Royal, 4.30.
- Chemical, 8. "Temperature of Certain Flames," by W. N. Hartley, F.R.S. "Halogen Additive Products of Substituted Thiosinamines," by Augustus E. Dixon, M.D. "Constitution of Cereal Celluloses," by C. F. Cross, E. J. Bevan, and Claud Smith. "Apparatus for the Detection of Boric Acid," by W. M. Doherty. "Ethereal Salts of Optically Active Malic and Lactic Acids," by Prof. Purdie, F.R.S., and S. Williamson, Ph.D.
- Royal Institution, 3. "Recent Chemical Progress," by Prof. Dewar, F.R.S.
- FRIDAY, 24th.—Royal Institution, 9. "The Circulation of Organic Matter," by Prof. G. V. Poore, M.D.
- Physical, 5. "Symbolism in Thermodynamics," by R. A. Lehfeldt. "Adjustment of the Kelvin Bridge," by R. Appleyard. "The Effect of Wave-form on the Alternate Current Arc," by J. Frith.
- SATURDAY, 25th.—Royal Institution, 3. "The Vault of the Sixtine Chapel," by Prof. W. B. Richmond, R.A.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1900.

ON THE USE OF NON-UNIFORM MAGNETIC FIELDS IN PHOTOGRAPHY WITH THE X RAYS.

By GEORGES MESLIN.

I HAD recently the honour of submitting to the Academy the principle of a method destined to abridge the duration of exposure in photography by the X rays. We have seen that it is possible not merely to displace the active fluorescent spot, but to condense it so as to increase its brightness. This condensation is obtained by concentrating the cathodic rays which give rise to it, and this concentration is due to the fact that the field employed is not uniform. It is therefore necessary that the field should present a suitable variation to obtain the desired deformation.

On studying the influence of the variation of the field, both as regards its intensity and its form, we find that:—

1. On operating, e.g., with a horizontal tube and throwing back the cathodic rays towards the upper part of the terminal caps, there is a concentration in the middle vertical plane if the field is decreasing upwards, and an expansion if the field is increasing downwards; there is no variation in dimension if the field is uniform. It is necessary if we employ this arrangement to place the poles below the axis to obtain a suitable variation of the field.

2. We find also that on acting upon the rays in the neighbourhood, so as to throw them back upon the upper horizontal portion of the tube, it is important (to obtain a contraction in the other direction) to employ those parts where the lines of force turn their concavity upwards; the field then fulfils the duty of a cylindrical mirror, and we have a luminous horizontal line in the vertical median plane. We may then condense it in the other direction by increasing the mean intensity of the field.

By utilising these considerations, I have obtained in five seconds a photograph of the bones of the hand of an adult. It was possible to recognise on this proof the traces of a fracture of old date.—*Comptes Rendus*, cxxii., p. 776.

ON THE RAYS OF RÖNTGEN ELECTRIFIED.

By A. LEFAY.

IN a recent memoir which I have had the honour of submitting to the Academy, I gave a description of an experiment which has enabled me to show the deflection by the magnet of the Röntgen rays modified by a previous passage through an electrified lamella. I now propose to indicate some complementary results relative to these modified rays, which, as an abridgment, I propose calling "Röntgen's electrified rays."

If, instead of electrifying these rays by putting in communication the metallic lamella with the negative pole of the induction coil, as I have indicated in the experiment above described, we take as the source the negative pole of a static machine, we observe a deflection in the same direction as that which I have already spoken of. It is no longer the same if we electrify the lamella positively with the same machine; the direction of the deviation is then inverted.

I had in the first place obtained this last result by taking as a source of electricity the positive pole of the Ruhmkorff coil which actuates my Crookes tube; but it

appeared so strange to me, that before announcing it I wished to verify the fact that it is equally produced on employing a source of static electricity.

There exist, therefore, Röntgen's rays electrified both positively and negatively.

The research into the laws which connect the magnitude of the deviation to the intensity of the magnetic field, to the state of electrification of the lamella, and to the nature of the dielectric will form the subject of a more extensive investigation. For the present I must confine myself to the foregoing qualitative indications, pointing out that there must exist between the Röntgen rays electrified negatively and propagating themselves in rarefied air and the cathodic rays the greatest analogy, *perhaps even absolute identity*.

It is convenient, in order to retain the direction of the deviations, to employ the very suggestive procedure devised by Hittorf with reference to the cathodic rays. Let us assimilate the Röntgen flux to a sheaf of conductive wires, indefinite, flexible, and without weight. When they traverse a plate positively electrified, they permit its discharge, and are the seat of an electric movement which flows towards the points with the lowest potentials. When the lamella is electrified positively, the direction of the movement is inverse. In both cases these conductors twist under the action of the magnetic field, and the direction of the deviation is given by Ampère's rule.

I conclude this paper by indicating a fact of a quite different order, though not without interest. It has been remarked that in certain Crookes tubes the degree of the vacuum increases gradually, and that such tubes before long cease acting. This accident happened to my tube about a month ago. I then had the idea of placing it for some time in a stove at 200°, which restored its original properties. Since that time I have continued to make use of it, re-heating it when it began to show signs of weakness. This practical observation perfectly corroborates the recent communication by M. Goury relating to the occlusion of gases by the glass of the Crookes tubes.—*Comptes Rendus*, cxxii., p. 809.

ON THE DIFFERENT PROPERTIES OF THE INVISIBLE RADIATIONS EMITTED BY URANIUM SALTS, AND THE RADIATION OF THE ANTIKATHODIC WALL OF A CROOKES TUBE.

By HENRI BECQUEREL.

THE study of the properties of the radiations emitted by the salts of uranium, on which I have already discoursed to the Academy in the foregoing sessions, and to which have to be added some new properties described below, renders it possible to establish important differences between the effects of these radiations and the effects produced by the radiation of the antikathodic wall of a Crookes tube, such as Prof. Röntgen has described and applied.

1. Double Refraction. Polarisation and Dichroism through a Tourmaline.

With the purpose of examining if the radiations emitted by the salts of uranium are polarised, I arranged the following experiment:—A slender slice of tourmaline, cut parallel to the axis, and of 0.50 m.m. in thickness, was cut in two; the two halves were juxtaposed so that their axes were rectangular, and the whole was covered by a single plate, parallel to the axis, of 0.88 m.m. in thickness, and the axis of which was parallel to the axis of one of the two halves of the original tourmaline. In these conditions ordinary light is transmitted through the two

tourmalines (the axes of which are parallel), and is arrested through the other half of the system. This total, thus arranged, was placed on a photographic plate, previously wrapped in black paper, and was covered with a lamina of the double uranyl and potassium sulphate. The photographic plate, developed after the lapse of sixty hours, showed very distinctly the silhouette of the tourmalines, and the action through the parallel tourmalines was notably stronger than that through the crossed tourmalines.

This experiment shows therefore at once, for the invisible rays emitted by uranium salts, the double refraction, the polarisation of the two rays, and their unequal absorption through the tourmaline.

The same experiment, repeated with the same tourmalines and the radiation emanating from a Crookes tube, gave a negative result; the two flat layers have absorbed the radiation equally. This result, which has already been signalled by Prof. Röntgen, is in agreement with the absence of appreciable radiation. It does not prove the radiation is not polarised, but merely that the absorption is the same for parallel tourmalines as for crossed tourmalines.

2. Unequal Absorption for different Substances.

The absorption of the two radiations which occupy us, when they traverse the same substances, presents very different characters. We may demonstrate this either by the photographic method, which gives qualitative results, or by the electroscope, which furnishes the relative measurements.

a. Photographic Method.—If we project the radiation of a Crookes tube upon a photographic plate wrapped in black paper, and covered with different substances in thin slices, or with small flat tubes filled with different liquids, we observe at first that on a short exposure most substances—except paraffin, which is very transparent, and aluminium, which is a little less so—behave as having opacities very close together. Still we find that water is much more opaque than paraffin, and a solution of uranium nitrate is more opaque than solutions of copper nitrate and gold chloride.

If we expose for a longer time we find that a plate of copper of 0.04 m.m. is traversed, but at a thickness of 0.05 m.m. copper is very sparingly transmissive. Platinum, of the thickness of 0.08 m.m., appears one of the most opaque of the bodies studied. On the same plates there were also zinc, lead, silver, glass, spar, quartz, rock-salt, &c. Glass of 2.13 m.m. in thickness, quartz perpendicular to its axis (2.05 m.m.), spar (1.93 m.m. and 2.40 m.m.), and rock-salt, appeared as little transparent as copper.

The absorption of rays emitted by a salt of uranium is very different. Aluminium and paraffin are always very transparent, but the metals are much more easily traversed by the radiation of a Crookes tube; copper (0.10 m.m.) is very transparent; platinum (0.08 m.m.) equally, but a little less than copper; silver also transmits these radiations, as does zinc; lead (0.36 m.m.) behaves as opaque.

Quartz (4.66 m.m.) and Iceland spar (4.48 m.m.) are very slightly transparent; sulphur (2.01 m.m.) is more so.

We perceive already that the radiations emitted by the salts of uranium traverse the majority of bodies more easily—especially metals—than does the radiation of a Crookes tube.

b. Electroscopic Method.—The discharge of a substance electrified by the radiations having traversed various screens leads to the same conclusion. I have already shown that quartz absorbs less the radiations of the salts of uranium than the radiation of a Crookes tube.

If we cause a Crookes tube to act upon the gold leaves of an electroscope, a plate of aluminium of 0.10 m.m. in thickness transmits an intense radiation, and the collapse of the gold leaves ensues in a few seconds; if we then interpose a plate of copper of 0.10 m.m. in thickness, the gold leaves cease to approach each other, or at least ap-

proach each other extremely slowly. Platinum intercepts the radiation still more.

It is not the same with the rays emitted by the salts of uranium, which traverse copper and platinum much more easily. I give here certain figures measuring the action through these two metals. The experiment was arranged as follows:—A lamella of the double uranyl-potassium sulphate was placed at about 2 c.m. below the gold leaves of the electroscope. I studied then the loss of the latter when this lamella acted alone, or on interposing successively or simultaneously screens formed of sheets of aluminium, copper, or platinum. The sheet aluminium was 0.10 m.m. in thickness, the sheet copper 0.09 m.m., and the sheet platinum 0.035 m.m. The action was measured by the speed of the collapse of the gold leaves, or by the fraction of a degree by which their angle diminishes per second; we know that this decrease is sensibly proportional to the time. The following numbers express the velocities in seconds of an angle and in seconds of time.

Action of a Plate of the Double Uranyl-Potassium Sulphate on the Gold Leaves of an Electroscope.

Nature of screens.	Date and mean hour of movement.	Velocity of collapse
Without screen	Mar. 28, 1.45 p.m.	28.18
Aluminium screen (0.10 m.m.) ..	" 3 ..	9.42
Copper do. (0.09 ") ..	" 3.50 ..	11.40
Platinum do. (0.035 ") ..	" 5 ..	9.60
Platinum and aluminium superimposed	" 5.50 ..	6.53
Without screen	" 6.20 ..	33.60
Aluminium and copper superimposed	" 6.40 ..	7.44
No screen (next day)	Mar. 29, 5.40 ..	33.00

It is perceived that copper and aluminium have approximately the same absorption for the same thickness, that platinum absorbs rather more, and that the absorption of superposed screens is less than the sum of the effects due to each, as in Melloni's experiments on thermochrosis, and as it has been established by Hurmuzescu and Benoist by antikatodic radiation.

The radiations emitted by the lamella of uranium salt are not homogeneous.

In an experiment made last week I observed that the electroscope discharges itself through a screen of copper of 1.40 m.m. in thickness.

The above figures show also that, a short time after exposure to light, the action of the lamella of the double uranium salt was a little stronger. In five hours there is produced a slight decrease, after which the action remains sensibly constant until the next day.

3. On some Peculiar Properties of the Emission of Radiations by the Salts of Uranium.

I have already pointed out the refractive independence of the invisible radiations of the uranium salts, and the emissions of visible radiations of phosphorescence; in particular the uranous salts which are not phosphorescent emit invisible radiations. I have also indicated that uranium nitrate melted, and, having been allowed to crystallise in the dark, was as active as the crystals of the same salt exposed to the light. I have recently satisfied myself that uranium nitrate, dissolved in water, is still as active, although this solution is not fluorescent. This is a new instance of the mutual independence of these two phenomena of emission.

I have likewise examined if these radiations might communicate a sensible phosphorescence to sulphides which had become inactive, or to various specimens of hexagonal blende which I possess. The result has been negative, at least as far as the immediate effect is concerned. In like manner the action of the radiation of a Crookes tube communicates no activity to hexagonal blende, either during the excitation or afterwards on prolonging the exposure during three days.

I have not observed any appreciable difference between the activity of a lamella of the double uranyl-potassium sulphate exposed to the radiation of a Crookes tube and a lamella not exposed. During the direct influence of this radiation upon a photographic plate, the lamella behaves as if opaque. It has then been placed upon another photographic plate, by the side of a lamella of the same salt, and the two lamellæ have given identical impressions.

I must still cite an experiment which seems in contradiction with the phenomena of reflection and refraction which I have observed.

Between two lamellæ of glass of the same thickness (1·83 m.m. in one experiment and 1·37 m.m. in the other) I heaped up powder of glass obtained by pulverising a piece of the same glass, and the powder slightly heaped up dusted the surface of the glass plates. Under these conditions the band of pulverised glass appeared as if opaque to ordinary light. It is known that the radiation of a Crookes tube traverses it with the same facility as a plate of homogeneous glass: this is one of the fundamental experiments of Prof. Röntgen. In the conditions just indicated, and with the radiations emitted by the salts of uranium, the band of powdered glass behaved as strikingly more transparent than the adjoining glass plates. As the quantity of matter traversed is sensibly less, we cannot deduce any certain conclusion from this contradictory experiment.

4. General Considerations.

It would be premature to draw absolute conclusions from the foregoing experiments. If we regarded only the simple phenomena of absorption, we might render an account of the facts by admitting that the radiations emitted by the uranium salts and the radiation of a Crookes tube behave as having different wave-lengths, but the absence of reflection or refraction well established for the radiation studied by Prof. Röntgen establishes a more profound difference. It seems more probable to think that the phosphorescence of the antikathodic spot is only a phenomenon concomitant of an electric phenomenon of which it is the seat, and that it is this electric phenomenon—a sort of effluve, as it results from the experiments of H. Dufour (*Comptes Rendus*, cxxii., p. 460), which provokes the phosphorescence of the photographic plate, and in consequence the reduction of the silver salts by the phosphorescent radiations excited on the spot. As for the phosphorescence of the glass of the Crookes tubes, it is possibly accompanied by radiations analogous to those emitted by the salts of uranium, but a very long exposure would be needed for their manifestations. — *Comptes Rendus*, cxxii., p. 762.

THE STORAGE CELL OF THE FUTURE: A NON-SULPHATING PHOSPHO-ACCUMULATOR.

By H. N. WARREN, Research Analyst.

In this improved form of cell, the old method of using red-lead or peroxide is entirely dispensed with, each plate being composed of pure spongy lead, obtained by pasting lead grids of special construction with a paste composed of litharge and phosphoric and sulphuric acids; drying the so-prepared plate for several hours at a temperature of about 250° F.; further treatment of the same with acids, and continued drying, until finally a biscuit plate is obtained. The plates are next arranged in pile fashion, with alternate plates of amalgamised zinc interposed between the leads, and insulated from each other by means of small carbon blocks, the pile thus formed being immersed in a solution of dilute vitriol. A somewhat violent reaction at once takes place, a copious evolution of gas is given off from the lead plates, and continues so until perfect reduction terminates the action,

the result being a fine porous lead plate, which, after washing to free it from accompanying zinc salts, is most admirably adapted for the further process of forming, which is brought about by insulating the plates by means of suitable material, and actuating upon them with an electric energy varying in quantity as to the size of the plates to form.

The plates now in communication with the positive electrode will, by this treatment, be noticed to have speedily assumed a brown tint, which rapidly increases until the whole of the spongy lead contained therein is converted into peroxide, while at the same time the negative element will be found, upon close examination, to be possessed of a somewhat lighter tint and closer texture.

The plates, having been now perfectly formed, are next rendered non-sulphating, by soaking the same in dilute phosphoric acid, or 12 per cent of the same acid may be advantageously introduced into the dilute vitriol bath in the first instance. Plates formed by this treatment will be found to compare most favourably with any others upon the market, being formed in less than half the time, and also, at the same time, being capable of resisting sulphation.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

ARSENIC IN COAL.

By W. M. DOHERTY, F.C.S., Government Laboratory, N.S.W.

In a recent trial in Sydney connected with an arsenical poisoning case, a rather unusual matter was introduced. It was alleged that the person accused of administering the arsenic disposed of the balance in his possession by burning it in a kitchen stove. To ascertain if there was any truth in this allegation, certain samples of soot, flue-dust, ashes, &c., were procured from different parts of the stove, the stove-pipe, and the brick chimney into which the stove-pipe led. These were tested by the Government Analyst for N.S.W., who found in the mixed flue-dust and soot taken from a position in the stove between the fire-place and the pipe that arsenic was present to the extent of 8 grains to the pound of the mixed flue-dust and soot. The soot from the stove-pipe, and also that from the brick chimney, were separately analysed, and traces of arsenic were found in each case. Coal was the fuel used in the stove. It was suggested that the presence of arsenic in soot taken from a place where coal had been burned was not necessarily an indication that arsenic had been added to the fire from some extraneous source, since it is highly probable that arsenic exists naturally in some portions of all coal seams. Therefore, it may have found its way into the kitchen stove in the most innocent manner. It was argued by some scientific men that as it is not uncommon to find strong traces of copper, lead, and other metals, besides occasionally even considerable quantities of sulphide of iron, it is most likely that arsenic may also be present at times in coal. But this argument seemed to lose much of its significance when applied to this particular case; the relatively large proportion of arsenic found in the flue-dust pointed to the conclusion that it did not come naturally from coal, however else it may have come.

There was no available recorded instance of the presence of arsenic in coal; and, so far as I am aware, the question had not yet been touched. In order, then, to discover if it were possible to trace arsenic in New South Wales coals, I obtained various samples of soot taken from flues where coal had been burned for years, and by the kindness of several gentlemen connected with the coal trade, I have been able to test samples from the following mines, which I think fairly represent the coal seams of the colony:—The Vale of Clwydd, Great Southern, South Bulli, Metropolitan, Newcastle-Wallsend, and Greta.

After a series of experiments, and repeated searching analysis, in no instance could I find the slightest trace of arsenic in the samples mentioned.

The work I have been able to contribute to this subject will not, of course, settle the question definitely as to the entire absence of arsenic in all coals; yet it may have a value, inasmuch as it shows that a large number of samples, selected indiscriminately from a number of coal mines, contain absolutely no arsenic.

It should be mentioned that in two instances I found copper and lead; and, in some of the samples, also comparatively large quantities of brassy, which, on separate examination, were found to be arsenic free.

The methods used in the investigation were oxidation with hydrochloric acid and potassium chlorate, and distillation with hydrochloric acid and ferrous chloride. As final tests, the methods of Marsh and Reinsch, and an excellent arrangement of Mayencon and Bergeret's highly sensitive perchloride of mercury test, designed by Mr. W. M. Hamlet, F.I.C., F.C.S., were used in all cases.

As a check on the reliability of the processes, control experiments were made by adding five m.grms. of white arsenic to a weight of coal equal to the quantity operated on (*i.e.*, 100 grms.), and it was repeatedly found to give marked indications of its presence.

ON CEMENTED OPEN-HEARTH OR BESSEMER STEELS.

By SERGIUS KERN, M.E., St. Petersburg.

We cannot certainly venture to say that we were the first to propose the use of open-hearth or Bessemer steels, in the preparation of cemented steel, for the production of special qualities of crucible steel. Anyhow, our short notice on this subject, giving some details of our experiments, appeared in the Russian mining paper *Gorny Listok*, No. 14, 1892.

After successful results in our several times interrupted experiments, we expect to have means for considerable experiments on our process of crucible steel method this coming summer, and we give some few notes on the method which in details is entirely new.

Soft open-hearth steel, containing not more than 0.25 per cent of manganese, phosphorus + sulphur 0.04 per cent, in the form of rolled flat bars ($1\frac{1}{2}'' \times \frac{3}{4}''$), is sheared into bits, $1\frac{1}{2}''$ to $2''$ in length, which are cemented in quantities, by using small cementation furnaces. Where re-heating and puddling furnaces are in constant work, the waste heat of such furnaces may be used in a special way.

The resulting cemented steel containing from 0.85 to 1.15 per cent of carbon, is assorted, and used for the production of special qualities of crucible steel (tools, projectiles, chief parts of ordnance, &c.).

Our process consists in melting such cemented steels, sometimes with a small quantity of wrought iron, and with the additions of certain small quantities of rich silicon iron and chrome ironstone.

The following analysis of a chisel for cold metal working gives an idea of the steel obtained by our process:—

	Per cent.
Carbon	0.95
Manganese	0.30
Phosphorus + sulphur ..	0.04
Chromium	0.12
Silicon	0.27

The metal, containing little manganese and impurities, hardens evenly, without cracking. The double-hardening (*double-trempe*) acts beneficially on this steel.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 184.)

With the object of finding out whether it was possible, by means of pure chloride or oxide of barium, to cause the appearance of one of the characteristic lines of the electric spectrum of calcium or strontium, and especially of the prominent blue lines common to the flame and electric spectra,—in other words, whether barium could be resolved into calcium and strontium, I eagerly profited by the opportunity afforded me by M. Duboscq of making an experiment, on a very large scale, with the electric light plant at Brussels, using either a battery or a dynamo. For this purpose I volatilised, with the help of M. Duboscq, who supervised all the installations, and of M. Romme-laere, some chloride and oxide of barium in the voltaic arc produced in succession by fifty, one hundred, and two hundred very large Bunsen cells, and in the electric arc from a 10,000 c.p. dynamo.

To carry out these experiments, I had to put one end of two pure carbon rods, 10 c.m. long by about 1 c.m. diam., into, and thoroughly coat them with, pure fused chloride or oxide of barium.

These rods were held upright by one end in strong insulated copper clips, 25 c.m. apart, working by means of a rack, with an insulated handle, on a varnished glass stem attached to a thick sheet of plate glass, also varnished. The upper rack was connected to the negative pole, the lower to the positive pole of the battery.

The upper rod, pointed at its free lower end, was adjusted so that its point was exactly in the centre of a cavity in the upper end of the lower rod. This cavity would hold about 1 gm. of fused chloride or oxide of barium.

By means of the insulated racks it was possible, without breaking the insulation, to put the electrodes in contact so as to destroy the arc, or to part them, and so lengthen or vary the diameter of the arc formed by the current already established.

The stem carrying the rods arranged in this manner was placed at a suitable distance in front of the slit of the spectroscope. This distance varied between two and three metres, according to the instrument used.

I adopted the above-described arrangements, because I wished to fix the position of the electrodes, both for examining the electric arc charged with baryta, the electrodes being kept apart, and to examine the light produced by contact of the electrodes in the presence of a barium compound.

Now this condition of absolute steadiness was difficult, if not impossible, to obtain with the regulators I had at my disposal. In fact, in these regulators the electrodes were continually in motion, either approaching till they touched or receding to the limiting length of the arc. It follows from these oscillations that, when using fixed spectroscopes, one is examining a continually varying luminous point; within very small intervals, one sees successively the spectrum of the electrodes in contact, the spectrum of a very short but thick arc, and the spectrum of a long thin arc,—spectra whose constituents are different, but which may be mistaken one for the other on account of the phenomenon of persistence.

Whereas by my arrangement I could, by working the rack, after having established the current (by putting the electrodes in contact, and heating their ends in an oxy-hydrogen blowpipe, so as to fuse the chloride or oxide of barium), adjust the electrodes so as to make the axis of the collimator coincide either with the middle of the arc or with the electrodes in contact.

As regards the barium spectrum, the results were the same. For example, when examining with the Steinheil spectroscope a baryta arc, either short and thick or long

and *thin*, it was impossible to see, for a single moment, in the spectrum, the blue and violet calcium and strontium lines.

When using the Duboscq spectroscope fitted with five prisms, and taking the solar spectrum as a standard, the eye was not able to perceive in the barium arc spectrum, or in the spectrum of the bright light produced by the contact of the electrodes moistened with the chloride of barium, the blue calcium line, and the blue and violet strontium lines in the position they ought to occupy in the solar spectrum.

On making the slit very narrow, and only allowing a pencil of light about two or three m.m. high to pass through it, so as to obtain a spectrum about 1 c.m. high, bounded by two dark bands, we made the following observations:—

A. Spectrum analysis of an arc gave a spectrum which was more strongly illuminated when the arc was short.

Whatever the degree of luminosity, the spectrum consisted of a continuous spectrum, on which appeared:—

- 1st. The barium spectrum as it was seen in a spark without a condenser, charged with barium.
- 2nd. The electric arc carbon spectrum, consisting of fine lines more strongly coloured when the arc was short.

B. Spectrum analysis of the bright light formed by the electrodes in contact, and entirely surrounded by baryta vapours, showed a very bright spectrum, consisting of a continuous spectrum, on which appeared only the electric barium spectrum as it was seen in the arc, side by side with the fine carbon lines.

When the slit is sufficiently narrow, and the distance between the electrodes and the analysers properly adjusted, the electric barium lines can be distinguished so perfectly that it is easy to measure the position of each of them in the spectrum, but excessively fatiguing to the eye on account of the bright illumination of the continuous spectrum.

Following the revision of my spectroscopic researches in collaboration with M. Depaire, I tried to check my research on the arc spectrum of barium. We used a current produced by the Julien accumulators, and also by the Gramme and Siemens dynamos coupled.

The spectroscopes used were:—

- 1st. One with flint-glass prisms made by M. Duboscq, the same as that used by M. Lecoq de Boisbaudran for his work.
- 2nd. One with two half prisms and lenses of quartz, made by M. Hilger.
- 3rd. The new direct-vision instrument designed by Messrs. Liveing and Dewar, also made by M. Hilger.

We used a Gérard regulator to carry the electrodes. The pure carbon rods were ten c.m. long by about one c.m. diam. The lower end of the upper rod was pointed; the upper end of the lower rod was hollowed to contain about 1 grm. of fused chloride or oxide of barium.

When looking through the spectroscopes, at a suitable distance in front of the electrodes, we saw exactly the same phenomena as those described above, that is to say:—

- 1st. Spectrum analysis of the barium arc, whatever its length or diameter, showed a very bright continuous spectrum, on which was superposed both the electric spectrum of barium, well known through Bunsen's researches, and the fine electric carbon lines such as have been drawn by M. Fievez, without any trace of the blue and violet calcium and strontium lines.
- 2nd. Spectrum analysis of the bright light produced by the electrodes in contact, surrounded by vaporised barium compounds, showed a continuous spectrum, on which was superposed the electric spectrum of barium only.

Owing to the oscillation of the carbon electrodes in the Gérard regulator, both the above-mentioned spectra were seen alternately, so long as all the chloride or oxide was not volatilised or dispersed too much by the current.

By introducing either chloride or oxide of barium into the arc, by means of a pure carbon spatula of suitable size, and interposing a piece of blue glass between the eye and the arc, so as not to strain the eye, it was possible to see the barium compound melt as soon as it was introduced into the arc, and take a spheroidal form. The spheroid floated in the arc until it was completely volatilised, or, as frequently happened, until it was thrown against the negative electrode, along which it was spread in small drops and scattered to some distance.

By repeating this operation frequently, and analysing the barium arc, whilst it lasted, the stability of the electric barium spectrum under the conditions of the experiment was demonstrated.

It follows from the above that there is no connection between the barium spectra and the spectra of sodium, potassium, lithium, calcium, and strontium.

During the course of the researches I have just described, it has happened that I have met with—either in the flame spectrum or the electric spectrum of a barium compound—fugitive traces of the blue lines due to calcium and strontium. When this occurred I was always able to separate, by chemical methods, the impurity detected by spectrum analysis. The fact of having been able to effect the separation and of simplifying it, by reducing the flame and electric spectra to constant forms, proves the elementary character of barium.

If this truth had need of further proof, the work I carried out with potassium, lithium, calcium, strontium, and barium furnished me with plenty of evidence.

(To be continued.)

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, April 10th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 2nd to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined all were recorded as clear, bright, and well filtered.

We have this month to record an excess of rainfall, after the long period of deficiency since November, 1895; the measured fall at Oxford being 2.45 inches, the 30 years' average 1.50 inches, showing an excess of 0.95 inch.

In spite of this increase of rain, and consequent flooding

of the river, the quality of the water is practically the same as of late, viz., excellent.

Our bacteriological examinations give the following results:—

	Colonies per c.c.
Thames water, unfiltered	2160
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	72
Ditto ditto lowest	16
Ditto ditto .. (12 samples) mean	41
New River water, unfiltered	1938
New River water, from the Company's clear water well	27
River Lea water, unfiltered	1900
River Lea water from the East London Com- pany's clear water well	29

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 19th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MR. HUGH CANDY was formally admitted a Fellow of the Society.

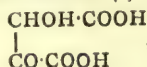
Certificates were read for the first time in favour of Messrs. W. Goodwin, 9, Westminster Gardens, Hillhead, Glasgow; Edgar Hawkins, M.D., Dudley Dispensary; Robert Haslewood Jones, 8, St. Mary's Place, Newcastle-on-Tyne; John McCrae, jun., 264, Calhoun Street, Cincinnati, Ohio; Thomas William Pilley, 33, Grove Hill Road, Denmark Hill, S.E.; Robert Barnabas Pollitt, care of Oscar Guttman, Esq., 12, Mark Lane, E.C.; Otto Rosenheim, 68, Belsize Park Gardens, N.W.; Walter Dalrymple Severn, 9, Earl's Court Square, S.W.; John Christopher Stead, 42, Grove Green Road, Leytonstone; Edward Channing Wills, Abbey Park, Keynsham, Bristol.

Of the following papers those marked * were read:—

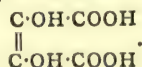
*37. "*The Constitution of a New Organic Acid resulting from the Oxidation of Tartaric Acid.*" By HENRY J. HORSTMAN FENTON, M.A.

This paper gives an account of numerous experiments which the author has recently made with a view of investigating the constitution of the new acid, $C_4H_4O_6$, obtained by the oxidation of tartaric acid in presence of iron, which has been described in former communications.

The molecular weight, basicity, and several characteristic relationships of the acid having been already established, a choice is left between (1) the ketonic formula—



and (2) the dihydroxylic formula—



The acid might assume both forms, or, if represented by the second formula, a fumaroid and maleinoid modification would be expected. The following is a brief summary of the principal results obtained:—

The absence of a ketonic group is demonstrated by the behaviour of phenylhydride and of hydroxylamine. These agents have no action whatever upon the methyl and

ethyl esters, and the crystalline compounds which they produce with the free acid are shown to be the respective normal salts.

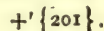
The presence of two alcoholic hydroxyl groups is shown by the actions of acetyl chloride, benzoyl chloride, and acetic anhydride, and the unsaturated nature of the acid is indicated, directly or indirectly, by several of its reactions. These facts leave no doubt that preference must be given to the second formula, and, on account of the great instability of the acid and normal aniline salts, and for other reasons, it is concluded that the acid belongs to the maleic series.

By the action of hydrogen bromide in acetic acid solution, an acid is obtained which has the same composition as the original acid, and many of its properties are similar. But its crystalline form is altogether different, and its acid aniline salt shows a much greater stability in aqueous solution. It is suggested that this product may be the corresponding dihydroxyfumaric acid, the formation of which could be readily understood from two intermediate compounds which have been isolated.

*38. "*The Volume and Optical Relationships of the Potassium, Rubidium, and Cesium Salts of the Monoclinic Series, $R_2M(SO_4)_2\cdot 6H_2O$.*" By A. TUTTON, Assoc. R.C.S.

In this communication are presented the results of a detailed investigation of the physical properties of the same 22 salts whose morphological relationships were described in a former memoir (*Trans.*, 1893, lxiii., 337). The main conclusions are as follows:—

1. The whole of the salts of the series exhibit a common cleavage direction parallel to the orthodome—



2. The relative density increases by an approximately constant amount for each of the two specific changes throughout the series, when potassium is replaced by rubidium, or the latter by cesium; the difference evoked by the former change is larger than that produced by the latter in the proportion of 5 : 4.

3. A similar constant increase occurs in the molecular volume, the replacement of potassium by rubidium being invariably accompanied by an increase of about 9·3 units, while the interchange of cesium for rubidium results in the larger increase of about 13 units. The determination of the molecular volume is almost exclusively a function of the alkali metal, change of the second metal being practically unaccompanied by any change of volume.

4. The replacement of potassium by rubidium, or the latter by cesium, is accompanied by a marked increase in the separation of the structural units along each of the axial directions. The elemental distance ratios of any rubidium salt of the series are consequently intermediate between those of the potassium and cesium salts containing the same second metal. The effect is greatest when cesium replaces rubidium.

5. The orientation of the variable axes of the optical indicatrix, lying in the symmetry plane, of every rubidium salt of the series, is intermediate between that of the potassium and cesium salts containing the same second metal. The replacement of rubidium by cesium is accompanied by a much greater change of orientation than the interchange of rubidium for potassium.

6. The refractive indices of any rubidium salt of the series are without exception intermediate between those of the corresponding potassium and cesium salts, and nearest to those of the potassium salt. An increase in the atomic weight of the contained alkali metal is accompanied by an increase of refractive power, and the increase in refraction becomes relatively greater as the atomic weight becomes higher.

7. The relative velocities of light vibration along the three axes of the optical ellipsoid of every rubidium salt of the series are intermediate between those along the corresponding directions in the analogous potassium and

cæsium salts. Increase in the atomic weight of the alkali metal is accompanied by an increase of resistance to the vibrations of light waves along each ellipsoidal axis, and this alteration is much the greatest when cæsium replaces rubidium.

8. An increase in the atomic weight of the alkali metal is accompanied by convergence of the values of the velocity along the three axial directions towards unity, and consequently by a diminution in the double refraction. This property is already feeble in the potassium salts, and it is extremely weak in the cæsium salts; the rubidium salts occupy an intermediate position in this respect.

9. Cæsium nickel sulphate differs from the other salts of the series in exhibiting negative double refraction, the usual sign being positive. This fact is directly due to the operation of the preceding rule; owing to the fact that in the potassium nickel salt the two nearest of the three values of the velocity are at their maximum separation for the series, the rule of progressive convergence causes it to happen that in the cæsium salt the third value has approached nearest the intermediate value, and this reverses the sign of double refraction. This interesting fact would have been inexplicable without the rule now established.

10. Another extraordinary result of the rule is afforded in the case of cæsium magnesium sulphate, where, owing to the separation of the two nearest values of the velocity being at its minimum for the potassium salts of the series in potassium magnesium sulphate, the progressive convergence actually results in those two values arriving at unity in the cæsium salt, which consequently exhibits simulated uniaxial refraction phenomena.

11. The whole of the specific and molecular optical constants, calculated by means of the formulæ of either Lorenz or Gladstone and Dale, for every rubidium salt of the series are intermediate between those of the potassium and cæsium salts containing the same second metal. An increase in the atomic weight of the alkali metal is accompanied by a diminution in the specific constants and an increase in the molecular constants, the former being greatest when rubidium replaces potassium, and the latter when cæsium replaces rubidium. These rules are independent of temperature.

12. Excluding the salts containing magnesium, for a reason connected with the statement in paragraph 10, the optic axial angle of every rubidium salt is intermediate between the optic axial angles of the analogous potassium and cæsium salts.

13. In the magnesium salts the progressive change proceeds as usual as far as the rubidium salt, but, owing to the extraordinary relations of the velocities of light vibration when the cæsium salt is reached, as stated in paragraph 10, cæsium magnesium sulphate exhibits specially interesting optic axial angle phenomena. The coincidence of two of the velocity values is only absolute for wave-length 450 in the blue, for which the uniaxial cross and circular rings are produced. Hence the salt exhibits very large dispersion in crossed axial planes for other wave-lengths, and great sensitiveness of the optic axial angle to change of temperature. These remarkable phenomena, almost unique as regards monoclinic symmetry, are the direct result of the rule regarding the velocity of light vibration.

14. A progressive alteration in the optic axial angle occurs upon rise of temperature, the rubidium salts being always affected in an intermediate manner.

15. So completely general are the rules given in the preceding paragraphs, that it is possible to predict the crystallographical characters of the two hitherto unprepared potassium salts of the series containing manganese and cadmium.

16. The final conclusion of the investigation is that the alkali metal R exerts a predominating influence in determining the characters of the crystals of this series, and the whole of the crystallographical properties of the

potassium, rubidium, and cæsium salts containing the same second metal M, are, in the case of every such group throughout the series, functions of the atomic weight of the alkali metal which they contain.

*39. "Comparison of the Results of the Investigations of the Simple and Double Sulphates containing Potassium, Rubidium, and Cæsium." By A. E. TUTTON, Assoc. R.C.S.

The author institutes a comparison of the whole of the experimental results derived from the investigations of the rhombic simple alkaline sulphates and of the monoclinic double salts of the series $R_2M(SO_4)_2 \cdot 6H_2O$. It is shown that the whole of the morphological and physical characters of the crystals of the rhombic normal sulphates of potassium, rubidium, and cæsium, and of any group of the monoclinic double sulphates of the series $R_2M(SO_4)_2 \cdot 6H_2O$, in which those simple salts of the three alkali metals are combined with the sulphates of either magnesium, zinc, iron, manganese, nickel, cobalt, copper, or cadmium, while exhibiting the same symmetry and the general similarities proper to isomorphous series, present well defined differences which are functions, and usually accelerating functions, of the atomic weight of the alkali metal which they contain.

*40. "The Bearing of the Results of the Investigations of the Simple and Double Sulphates containing Potassium, Rubidium, and Cæsium upon the Nature of the Structural Unit." By A. E. TUTTON, Assoc. R.C.S.

The author arrives at the following conclusions:—

(1) The absence of any considerable contraction in volume when the alkaline sulphate enters into the double sulphate, as contrasted with the relatively enormous contraction which occurs when the various atoms combine to form the chemical molecule of the alkaline sulphate, together with the facts that the double salt is only known in the solid crystallised condition, and that many of the individual members of the series are eminently unstable, render it highly improbable that there is chemical union between the molecular constituents of the double sulphates, and indicate that there is no necessity to assume linkage of any kind, but merely aggregation in accordance with such a type of homogeneous structure as ensures that they are always present in the same proportion. (2) In the production of crystals it is not necessary to suppose that any other structural units are concerned than the chemical molecules of the chemical compound in question or of the constituent chemical compounds in the cases of double salts or salts containing water of crystallisation, and the observed fact of the constancy of molecular proportions of the two latter is entirely accounted for by the nature of the type of homogeneous structure in which they find equilibrium. (3) The pedetic or "Brownian" motion of small particles, capillarity, convection currents, or any other slightly agitating forces which assist the chemical molecules to take up this condition of equilibrium necessary for the production of a homogeneous structure, will assist crystallisation. The molecular forces whose domain of action has been shown not to extend beyond a very few molecular distances, need only be concerned in maintaining the general cohesion. (4) Considering the chemical molecule as the structural unit, in general such units will not be endowed with the same symmetry as the crystal; it may have higher, equal, or lower symmetry according to the specific constitution of the molecule. This is in complete accordance with the generalisation of Barlow concerning the homogeneous portioning of space, and the conclusion of Fock derived from the theory of solid solutions. (5) The more heterogeneous the constitution of a crystallised substance, the lower in general is its type of symmetry. (6) The nature of the predominating faces, as being the planes most closely studded with similar "points," together with the directions of cleavage, agree in indicating that the type of homogeneous structure of the simple alkaline sulphates is that of the rectangular pinacoidal

prism, and that of the double sulphates the primary monoclinic prism, probably type 64a of Barlow. (7) The phenomenon of the rotation of the optical ellipsoid of the double sulphates, when the atomic weight of the alkali metal is changed, is completely accounted for by the acceptance of the above simple constitution for the double salts together with the suggestion of Barlow that the orientation of the optical ellipsoid is the resultant of a process of averaging the directional retardations experienced by light waves in traversing the homogeneous structure, due to the arrangement of the molecular matter. The greater amount of rotation when caesium replaces rubidium than when the latter replaces potassium, is thus the direct result of the correspondingly greater increase of volume, largely in a particular direction, which is observed.

*41. "*The Hydriodides of Hydroxylamine.*" By WYNDHAM R. DUNSTAN, F.R.S., and ERNEST GOULDING. The authors have isolated two hydriodides of hydroxylamine, $(\text{NH}_3\text{O})_3\text{HI}$ and $(\text{NH}_3\text{O})_2\text{HI}$, from the interaction of methyl iodide and a solution of hydroxylamine in methyl alcohol, these salts being formed in addition to the trimethylhydroxylamine hydriodide previously described (*Proc. Chem. Soc.*, 1894, 138). The normal hydriodide $(\text{NH}_3\text{O}\cdot\text{HI})$ could not be found. The same hydriodides may be formed by mixing strong aqueous hydriodic acid with the calculated quantity of hydroxylamine, dissolved in methyl alcohol. Both salts crystallise well, but when re-crystallised from methyl alcohol or from water, gradually lose hydroxylamine. The trihydroxylamine salt is the more stable, and may be preserved unchanged in dry air. Both salts are acid to litmus. All attempts to obtain the normal salt $(\text{NH}_3\text{O}\cdot\text{HI})$, by direct and indirect methods, have failed; its solution is very unstable and rapidly decomposes, iodine being liberated.

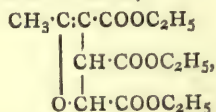
† 42. "*An Analysis of the Water from the Dropping Well at Knaresborough, in Yorkshire.*" By B. A. BURRELL.

The history of this remarkable spring is noticed at some length, from which it appears that its petrifying qualities were known in 1534.

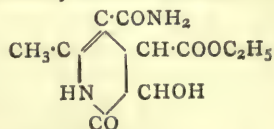
A complete analysis has now been made. The total solids amount to 162.435 grains per gallon, of which 114.37 grains are calcium sulphate, 25.48 calcium carbonate, and 17 magnesium sulphate. Traces of manganese and strontium were found.

43. "*Contributions to the Knowledge of Ethylic Acetoacetate. Part I. Acetonylmalic Acid.*" By S. RUHEMANN, Ph.D., M.A., and E. A. TYLER.

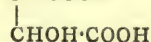
By the action of the sodium derivative of ethylic acetoacetate on ethylic chlorofumarate the authors find that the two stereoisomeric ethereal salts of the acetoacetic acids are not formed, but that in both cases one and the same compound of the formula,—



is formed, which is to be regarded as ethylic methylidihydrofurfurantricarboxylate (b.p. 188–189°, under a pressure of 15 m.m.). This constitution is supported by the chemical and physical properties of the substance. Ammonia reacts with the ethereal salt, forming a compound, which most probably has the formula,—



(m. p. 195°), whilst in the hydrolysis of the furfuran derivative, brought about by alcoholic potash, acetonylmalic acid,—



(m. p. 145–146°), is produced.

(To be continued).

NOTICES OF BOOKS.

Water Analysis. A Practical Treatise on the Examination of Potable Water. By J. ALFRED WANKLYN and ERNEST THEOPHON CHAPMAN. Tenth Edition. Revised and partially re-written by J. ALFRED WANKLYN, M.R.C.S., Corresponding Member of the Royal Bavarian Academy of Sciences (1869). London: Kegan Paul, Trench, Trübner, and Co. (Ltd.). 1896. Pp. 200.

PROF. WANKLYN'S treatise on the sanitary examination of potable waters is universally—and we may say on the whole favourably—known to sanitarians and analytical practitioners, and has appeared in French and German versions. As regards the process itself, little alteration has been made from the previous editions. The determination of the specific gravity of samples of water with the precautions now given will be recognised as a useful addition. No directions for the microscopical and bacteriological examination of waters have been given, the author holding that if the water is shown to be "dirty" by chemical examination, the failure to discover anything very alarming by a bacteriological examination should not justify its recommendation, whilst if it belongs to "the class of exquisitely pure waters" no bacteriological results are possible.

Mr. Wanklyn still attaches no especial value to a search for phosphates. But we must not infer—as has been erroneously done—that he ignores their presence in sewage, industrial waste waters, drainage, &c. His attention in this volume is confined mainly to potable waters. The possible presence of poisonous metals—we fear a growing evil—is very carefully considered. Chromium compounds, which may easily find their way into sewage, or even into potable waters, in districts where the dyeing, tissue-printing, and colour-making industries flourish, are not here overlooked, as has been too often the case in works on sanitary chemistry. The polemical matter, which in former editions was somewhat too prominent, has been very greatly reduced. But the most satisfactory feature in the edition before us will be found in the working details and practical hints which the experience of a quarter of a century has enabled the author to supply. On this account the work will be found highly valuable, even to those many analysts, medical officers of health, &c., who are fully acquainted with the broad outlines of the method as given in the earlier editions. Prof. Wanklyn considers—very justifiably—that lead in drinking-water, even to the extent of $\frac{1}{10}$ th grain per gallon, is dangerous, and should warrant its rejection as a municipal supply.

Elementary Practical Chemistry. A Laboratory Manual for Use in Organised Science Schools. By G. S. NEWTH, F.I.C., F.C.S., Demonstrator in the Royal College of Science, London; Assistant Examiner in Chemistry, Science and Art Department. London, New York, and Bombay: Longmans, Green, and Co. 1896. Crown 8vo., pp. 283.

WHAT are "organised schools"? A school without organisation is something difficult to conceive, whether its object be Science or word-mongering. But perhaps the term may have some special meaning familiar to the officials of the "Department."

"Formerly," we are told in the author's preface,

"students were taught chemistry in the lecture-room, the knowledge so gained being supplemented by a minimum amount of practical work." This is perfectly and lamentably true. But the tendency to make the student, from the very beginning, an investigator, was manifest in the teachings of Justus Liebig, and has been carried out in every German University long before it could find expression in any Syllabus of the Science and Art Department.

The experiments here prescribed are well selected for the purpose of making the student an observer, and of training him to draw accurate conclusions from the phenomena which he observes. Hence Mr. Newth's work, and the course of study therein laid down, will be well worth adoption in any Science school, even if it has the peculiarity of not being "organised."

CORRESPONDENCE.

ON A

MECHANICAL ACTION EMANATING FROM THE CROOKES TUBE ANALOGOUS TO THE PHOTOGRAPHIC ACTION DISCOVERED BY RÖNTGEN.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS of Feb. 28th (vol. lxxiii., p. 98) I notice an article with the above heading, by MM. Gossart and Chevalier. The article claims the discovery of a "new" force, manifesting mechanical action, and details an elaborate series of experiments with this new force, and promises more to follow. Doubtless the fundamental experiment of the article has long ago been observed by most, or all, users of Crookes tubes who had at hand also a "radiometer." The explanation of all that was observed by MM. Gossart and Chevalier is, I think, very simply found in electrostatic induction. Early in February, when I first set up a Crookes tube for X ray experiments, I observed that the radiometer had a decided tendency to a fixed position of the vanes; that the azimuth of this position changed on interposing an object *unsymmetrically* between the two tubes; that the vanes could be made to rotate in *either direction* by waving them around with a magnet, the finger, or other object—but the magnet was no better than the hand. It was, of course, *easier* to get continuous rotation in the *forward* direction of the radiometer, because the electrostatic induction and proper heat radiation then conspired, while they were opposed in the opposite case. I tried three tubes in order to thoroughly satisfy myself of the electrostatic nature of the force. One was a radiometer with mica vanes, the faces alternately blackened; a second was the same, except that the vanes were of aluminium; the third tube was the Crookes tube similar in appearance to a radiometer, except that all the faces of the vanes were bright, and it was provided with terminals; the vanes themselves to be made the cathode, in order to show "the mechanical effect of the reaction—or kick—of the charged molecules flying from the cathode." All the tubes presented the same general phenomena, about the only difference being that the last tube described, in the absence of any "radiometer" effect, would rotate in either direction with *equal* facility. When one can take off sparks from the Crookes tube in action, and even from objects near by, there is no need to invent a "new force" to affect a delicate radiometer vane.—I am, &c.,

JOHN DANIEL.

Vanderbilt University, Nashville,
Tenn., U.S.A.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Journal für Praktische Chemie,
New Series, Vol. lii., Part 16.

Our Knowledge of Flame.—M. Teclu.—This paper—a continuation, and which is not yet completed—requires the five accompanying figures. Concerning the colour of flames, the author remarks that, besides the luminous action of the ignited carbon liberated, we distinguish the primary colours yellow and blue, though not in a decided state of purity, from which, since the yellow occurs reddish, the mixed colours violet and green are produced in various shades; the yellowish red tone of colour is due to the hydrogen flame, and the bluish colour to the flame of carbon monoxide. These flames interpenetrate each other. The violet colouration of the margin of the flame is produced by the reddish tone of the hydrogen flame and the bluish tone of the carbon monoxide flame.

Researches from the Organic Laboratory of the Technical High School of Dresden.—E. von Meyer.—These researches include (III.) a paper on the "Action of some Diazo-compounds upon Cyanacetic ethylester," by B. Marquardt. This paper is not suitable for abridgment.

Compound Metallic Bases.—N. Kurnakow (Treatise second).—This paper, also, is not capable of abstraction.

Zeitschrift für Anorganische Chemie,
Vol. x., Parts 1 and 2.

Re-determination of the Atomic Weight of Zinc.—Theodore W. Richards and E. Folger Rogers.—The mean value found, assuming O=16, is Zn=65.404; if O=15.96, then Zn=65.240; and if O=15.88, then Zn=64.913. A part of this memoir has already appeared in the *Proceedings of the American Academy*.

Note on the Crystallisation of Bromine.—Henryk Arctowski.—Bromine obtained from solution in carbon disulphide by refrigeration below its point of saturation forms a heap of fine crystalline needles. Bromine obtained by refrigeration in a test-tube showed, on comminution, a distinct crystalline fracture and no striated surfaces. The lustre is not so decidedly metallic as that of iodine.

Crystallography of Mercurial Chloride.—Henryk Arctowski.—This paper requires the accompanying figure.

New Method of Quantitative Spectroscopic Analysis.—G. and H. Krüss.

Preparation of Tin Tetrachloride in Quantity.—Richard Lorenz.—This paper requires the accompanying figure.

Molybdenum Hydroxyl Chloride.—Ad. Vandenbergh.—This paper cannot be usefully reproduced without the four accompanying illustrations.

Determination of Phosphoric Acid by the Molybdenum Method.—H. Neubauer.

Study of Certain Potassium Fluorides and Oxyfluorides.—G. Marchetti.—The author obtains a normal fluoride containing no crystalline water, TiF_6K_2 , which on re-crystallisation from pure water is converted into $\text{TiF}_4 \cdot 2\text{KF} \cdot \text{H}_2\text{O}$. He also obtains molybdenum oxyfluoride, $\text{MoO}_2\text{F}_2 \cdot 2\text{KF} \cdot \text{H}_2\text{O}$ and $\text{WO}_2\text{F}_2 \cdot 2\text{KF} \cdot \text{H}_2\text{O}$. In these experiments he determines the fluorine according to the method of Penfield (CHEMICAL NEWS, xxxix., p. 179).

Conversion of Chlorine into Hydrochloric Acid.—Richard Lorenz.—The author suggests the lixiviation of ores with hydrochloric acid, after which the lixivium is concentrated and electrolysed. The anodic chlorine is

again converted into hydrochloric acid, which can be afresh used for lixiviating a proportion of ore. Little is to be found in scientific literature concerning the conversion of chlorine into hydrochloric acid by means of elevated temperatures.

Experiments for the Establishment of an Electrolytic Process for the Conjoint Production of Zinc and Lead.—R. Lorenz.—This memoir would require the insertion of the three accompanying figures. Some portions, however, describing the fractionated electrolysis of fused mixtures of metallic chlorides will be inserted in full.

Compounds of Selenium with Arsenic.—A. Clever and W. Muthmann.—The authors describe the production and properties of potassium oxyseleonoarsenate, of arsenpentaselenide, potassium metaseleonoarsenate, potassium sulph-seleonoarsenate, sodium oxyseleonoarsenate, sodium seleonoarsenite, sodium sulphoseleonoarsenate, potassium triselenide, and a new hydrate of sodium monoselenide.

Colour of the Ions as a Function of the Atomic Weight.—Julius Thomsen.—This journal has contained a memoir by Carey Lea on "The Relation of the Atom, the Ion, and the Molecule." The author arrives at the conclusion that the periodic system, hitherto accepted, seems worthy of rejection, as being founded upon erroneous principles," and he then proposes another system based on the colour of the ions. But the dependence of the colour of the ion upon the atomic weight appears very simple if we accept the form of the periodic system which I have published in the *Zeit. Anorg. Chemie* (vol. ix., p. 318). The dependence may be simply expressed in the following words:—"Only the ions of the mean members of the great series are coloured." The two first series, each with seven members, contain no coloured ions; the two next following, each with seventeen members, contain in each series seven to eight coloured ions (from titanium to copper, and from niobium to silver); and in the fifth series, with thirty-one members—some of them undiscovered—we find the group of the coloured ions (cerium to gold) in the middle; whilst colourless ions correspond in all the series to the exterior members.

MISCELLANEOUS.

Litmus Pencils.—We have much pleasure in giving publicity to a very useful and ingenious little appliance in the form of a "litmus pencil," shown in the accompanying woodcut. Its use is so obvious that comment is unnecessary. One half is red, and the other half blue; it only needs a couple of point protectors to make it



complete, and we have no doubt but that it will soon in great measure supersede the old form of books. To medical men it will certainly be a great boon, as it can be carried in the pocket and contains a practically inexhaustible supply of litmus always ready. Messrs. Christy and Co., of Lime Street, E.C., are the sole agents for England.

Iron and Steel Institute.—The Annual Meeting of the Institute will be held at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, the 7th and 8th days of May, 1896, commencing each day at 10.30 a.m. The following is a list of the Papers that are expected to be read and discussed:—"On the Rate of Diffusion of Carbon in Iron," by Professor W. C. Roberts-Austen, C.B., F.R.S. (Member of Council). "On some Alloys with Iron Carbides," by J. S. de Benneville (Philadelphia). "On Mond Gas as applied to Steel-making," by John H. Darby (Brymbo).

"On Hot Blast Stoves," by B. J. Hall (Westminster). "On the Hardening of Steel," by H. M. Howe (Boston); adjourned discussion. "On the Introduction of Standard Methods of Analysis," by the Baron Hanns Jüptner von Jonstorff (Neuberg, Austria). "On the Production of Metallic Bars of any Section by Extrusion," by Perry F. Nursey (London). "On Mr. Howe's Researches on the Hardening of Steel," by F. Osmond (Paris). "On the Treatment of Magnetic Iron Sand," by E. Metcalf Smith (New Zealand). "On the Making of the Iron Ores of Oxfordshire," by E. A. Walford, F.G.S. (Banbury).

Penetration of Gases into the Glass Sides of Crookes Tubes.—M. Gouy.—If we heat with the blow-pipe glass from a Crookes tube which has been in use for some time, it is seen to take a dull aspect, which at first makes us believe in denitrification. The alteration is confined to the interior surface of the tube; it is so much the more marked as the glass has received a more intense cathodic irradiation, and does not exist in those portions which have not been exposed. The microscope shows that this mat layer is especially formed of a multitude of gas bubbles, which are in the interior of the glass, but near its surface. On heating further these bubbles coalesce, increase in bulk, and finally become visible with the lens, or even to the naked eye. Thus glass which has been exposed to intense cathodic rays disengages numerous bubbles of gas when softened by heat. This phenomenon is not produced in any other case. It seems that the cathodic rays cause the gases of the tube to penetrate into the glass, where they remain occluded until set at liberty by the softening of the glass. These observations have been made with four tubes of glass somewhat different; one of them showed abundant bubbles only in the portions which had been most exposed to the cathodic rays.—*Comptes Rendus*, cxiii. P. 775.

Determination of Mercuric Salts by means of Sodium Peroxide.—Dr. R. C. Schuyten (*Chemiker Zeitung*).—I have previously stated (*Akad. Proefschrift*, Ghent, 1894) that sodium peroxide—a substance with oxidising properties—is capable of reducing sublimate to metallic mercury. Upon this behaviour I founded a method for the determination of mercuric salts which has the advantages of being quickly executed and of yielding accurate results. I have examined the following compounds with good results:—Mercuric chloride, mercurous chloride, mercuric sulphate, nitrate, and oxide (red). These substances, both in solution and suspended in water, are reduced first to yellow oxide, and then completely to metallic mercury. In the solutions filtered off from the precipitates no precipitation was caused by hydrogen sulphide. The determination was carried out

as follows:—In a porcelain capsule, which can be closed by a funnel, with a pipe bent at right-angles, the weighed substance is closed with a sufficiency of water. The sodium peroxide is then added by degrees until no further precipitate appears. The capsule is then closed with the funnel, and the liquid gently heated until the vapours condense in the tube; it is then allowed to cool, the funnel is well rinsed out, the metallic mercury is placed on a filter and weighed. During drying, the filter must be covered with paper, and the exsiccator placed in the dark at a low temperature. With sublimate purified by re-crystallisation I have obtained the following results:—Found, Hg, 73.54, 73.61, 73.41 per cent; calculated quantity, 73.92. In this case the halogen can be liberated by Volhard's method in the neutralised filtrate. Under the above conditions vermilion is not decomposed, even on ebullition, but this is the case in the organic mercurial addition products.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 13th inst., Sir James Crichton-Browne presiding. The following were elected Members:—Robert James Forrest, Major-General Sir Francis Grenfell, K.C.M.G., K.C.B., and M. W. Zambra.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8. (Cantor Lectures). "Applied Electro-Chemistry," by James Swinburne.
Medical, 8.30.
TUESDAY, 28th.—Royal Institution, 3. "Child-Study and Education," by Prof. James Sully, M.A.
Institute of Civil Engineers, 8.
Photographic, 8.
Medical and Surgical, 8.30.
WEDNESDAY, 29th.—Society of Arts, 8. "Fruit Drying or Evaporation," by Edward W. Badger.
British Astronomical, 5.
Geological, 8.
THURSDAY, 30th.—Royal, 4.30.
Royal Society Club, 6.30.
Institute of Electrical Engineers, 8.
Royal Institution, 3. "Recent Chemical Progress," by Prof. Dewar, F.R.S.
FRIDAY, May 1st.—Royal Institution, 5. (Annual Meeting). At 9, "Chronographs and their Application to Gun Ballistics," by Col. H. Watkin, C.B.
Geologists' Association, 8.
Quekett Club, 8.
SATURDAY, 2nd.—Royal Institution, 3. "The Vault of the Sixtine Chapel," by Prof. W. B. Richmond, R.A.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1901.

ON THE DIFFRACTION AND THE POLARISATION OF THE RÖNTGEN RAYS.

By G. SAGNAC.

I. To obtain real images of a luminous slit with a grating by transmission at equal intervals, we place it in front of a real image furnished by a converging sheaf of rays. We cannot do this with the Röntgen rays, which diverge on the exterior of a Crookes tube, and for which we have no lenses. To obtain real images of a slit I have diaphragmed the entrance into a large camera by a second slit, behind which is placed the grating.

I used a grate of $\frac{1}{10}$ m.m., constructed by M. Gaiffe, with platinum wires of nearly $\frac{1}{10}$ m.m. in diameter. The lower part of a luminous sheaf, defined by two metallic slits at the distance of 7.5 c.m., passes below the metallic mounting of the screen, and forms—on ground glass of the camera at 35 c.m. beyond the screen—a real image of the first slit. The upper part of the same sheaf traverses, at 2.5 c.m. behind the second slit, the screen placed at the incidence of 45° , which here augments the deviations and the intensities of the diffracted rays. These latter add to the direct image so many diffracted images, four of which are especially very distinct. These five images of the first slit, supposed to be rather narrow ($\frac{1}{4}$ m.m.), reinforce themselves by being partially superimposed, and form thus an image of a fluted aspect, broader by about 7 m.m. than the lower image without diffraction.

We regulate the parallelism of the edges of the slits among themselves and with the wires of the grating. For this purpose we realise the maximum distinctness of the diffraction fringes of the second slit illuminated by the former, rendered fine, then that of the shadows of the wires of the grating given by the second slit, rendered fine in its turn, the former being enlarged up to 1 m.m. We then enlarge the second slit until the shadows of the wires are seen to disappear.

For the source of light illuminating the slit we substitute a Crookes tube, and for the plate of ground glass a frame charged and closed. We have obtained a very well-defined proof.* We must seek to recognise in it the diffraction of a greater breadth of the upper image. If this image exceeds the lower image in breadth, such excess is certainly not more than $\frac{1}{4}$ m.m. It differs from the lower image solely by a width of 2 m.m. on each margin, where it presents seven appearances of fringes; but these apparent fringes correspond to the juxtapositions of the margins of the first slit given by the transparent intervals, to which the second slit limits on the screen the pencil of rays coming from each margin of the first slit.

Further, we substitute for the Crookes tube the flames of common salt, on exposing for about an hour with an open frame, and, using an orthochromatic plate (sensitive to yellow and green), we obtain a proof differing from the former by a fluted upper image enlarged by more than 7 m.m., even if we neglect the most intense parts of the margins. Now the appearances of five fringes of the former proof re-occur here between the broader flutings, as well in the last diffracted images as on the margins of the central image, and the simple nature of the light em-

ployed does not permit them to be considered as due to diffraction by the grating; they are certainly phenomena of shadows just explained. These same images of the margins of the first slit are certainly not very visible on proofs obtained with an open frame, either with ordinary gas-light or with the light of a Crookes tube, on account of the complication which the nature of the sources employed impresses on the diffracted flutings, especially if the sensitive plate is orthochromatic.

The expansion of the copper sheaf by diffraction, if it exists at all, does not exceed $\frac{1}{4}$ m.m. or scarcely $\frac{1}{4}$ m.m. Now an expansion of $\frac{1}{4}$ m.m., fourteen times less at least than that given by the light of the D ray, would correspond to a wave-length of 0.04 μ .

This enables us to conclude that the Röntgen rays which have acted on the sensitive plate through the wooden shutter of the frame do not possess wave-lengths exceeding a hundredth of a micron.

II. Are the Röntgen rays connected to a vector either longitudinally or transversely, and in the latter case how can they be polarised?

We cannot at present dream of polarising them by reflection, nor by refraction, nor doubtless by diffraction. Emission and diffusion might perhaps be tried. It is in any case simpler to attempt to polarise them by absorption. Let there be two crystalline plates, near to each other in thickness, parallel to the axis, superimposed with their axes parallel. Let us divide the surface of the upper plate in two halves, and cause one of them to turn by 90° . The system of the plates realises at once the analogue of the crossed tourmaline and of parallel tourmalines. With a monochromatic light the amplitude i becomes, when issuing from a plate, for the components perpendicular and parallel to the axis, respectively o and e , which differ if there is dichroism. The region of the principal parallel sections allows an intensity to pass, the excess of which over that of the other region is measured by $(o^2 - e^2)^2$.

Otherwise for the differences $(o - e)$ possibly of different signs, relative to different wave-lengths, the corresponding differences of intensity accumulate always in favour of the region where the principal sections are parallel.

I have sought if the effect is produced with the Röntgen rays when such system of three plates are arranged on the double black paper which covers the sensitive plate. The time of exposure was increased to several hours. The proofs obtained with the desirable intensity have not revealed a sensible dichroism.

Substances used.	Quartz.	Spar.	Brown Tourmaline.	Mica.	Potassium ferrocyanide.
	M.m.	M.m.	M.m.	M.m.	M.m.
Thickness of each plate	0.03	0.4	0.5	0.2	0.4 to 2

One precaution is indispensable to eliminate the influence of a small difference of nature, such as occurred in the tourmalines: we cause each of the two upper half-plates to turn on the spot by 90° , so that the regions of the principal parallel sections and of the crossed sections are mutually interchanged. A difference of intensity due to dichroism ought, in its displacement, to follow the parallelism of the principal sections. Now the very small difference of intensity perceived with the tourmalines always persisted in the same half-plate.

If the method admits of so easy a check, and is found independent of the complexity of the radiations employed, it is unfortunately not very sensitive. We see readily, in the case of light, that to detect a difference, e.g., of $1/10$ th between unity and the relation $\frac{o}{e}$, the photograph must

be able to show a relative difference of $1/50$ th between the luminous intensities which act upon two contiguous regions, which far exceeds that which may be hoped.

We cannot therefore derive from these negative experiments on dichroism an argument of great value in favour of the hypothesis of a longitudinal vector. They supply

* The Crookes tube manufactured by M. Chabaud has acted for eleven days, on an average five hours daily, without becoming sensibly weaker, and becoming heated less and less rapidly.

merely a further distinction between the X rays and the luminous rays which we know. — *Comptes Rendus*, cxxii., p. 783.

A CONDITION OF THE MAXIMUM OF POWER OF CROOKES TUBES.

By JAMES CHAPPUIS and E. NUGUES.

THE power of a Crookes tube, actuated by a Ruhmkorff coil with a Foucault interrupter, does not increase for one and the same intensity of current, measured in the closed inductor, in the same time as the number of interruptions.

We have measured this power with the electrometer of Hurmuzescu placed at various distances, and caused the number of interruptions to vary from 3 to 50, by the displacement of an additional weight on the oscillator. The following numbers show that for the coil experimented with there is a maximum reached near 10 interruptions:—

Number of interruptions.	Time of fall.	
3	27	47
6	23	—
10	20	24
25	30	34
50	37	42

The recent experiment on the emission of rays having a photographic power by means of fluorescent substances have led us to think that the visible fluorescence of the glass on the passage of the discharge may be followed by a kind of invisible fluorescence prolonging the photographic action. To verify this hypothesis we have made the following experiment:—

On the stem of the oscillator we fixed a thick plate of copper in which there had been made a slit of about 1 m.m. in width by 12 m.m. in height; a sensitive plate was placed behind and parallel to it, at the distance of 1 m.m. the source of light fitted with a diaphragm of 8 m.m. on the other surface of the metal plate at the distance of 16 c.m.

When the Foucault oscillator is set in motion, the rod carries with it, in its oscillatory movement, the slit over a course of 4 c.m., and at each double oscillation there is produced a fluorescence. We have caused the speed of the oscillator to carry from 3 to 20 interruptions per second, and the time of exposure from 1 to 30 minutes.

If the useful fluorescence is instantaneous, like the discharge which produces it, we ought to obtain a distinct image of the slit; if, on the contrary, it lasts a certain time, we ought to obtain a band giving at each point an indication of the photographic power of the tube at a corresponding instant.

In all cases we have obtained a distant image of the slit and of the movable plate; it would therefore be sufficient to convince ourselves of the inaccuracy of our hypothesis, to photograph the stem of the oscillator in movement; it gives, in fact, on our proofs a shadow with very definite edges.

We deposit a proof obtained by 36,000 passages of the slit.

The power of the tube is hence instantaneous, like the discharge which induces the fluorescence.

It seems to follow, from this experiment, that the power of the tube should be proportional to the number of the discharges; but, on the other hand, the length of the sparks which strike between the two bulbs of an exciter falls from 21 to 5 c.m. when the number of interruptions varies from 3 to 50.

There are then two phenomena which vary inversely, and which we must take into account for the production of the maximum power of the tube.

This maximum depends on the self-induction of the

induced coil, and the conditions necessary for its production vary, for one and the same current measured in the closed conductor, with the coil employed. Experiment alone permits it to be determined. — *Comptes Rendus*, cxxii., p. 810,

RESEARCHES ON THE EARTHS CONTAINED IN MONAZITE SANDS.

By P. SCHUTZENBERGER and O. BOUDOUARD.

WE have the honour of communicating to the Academy the continuation of our researches on the earths contained in the monazite sands, and especially in the salts, the double potassium salts of which are soluble in water saturated with potassium sulphate.

After treating the powdered mineral in heat with concentrated sulphuric acid, and eliminating the excess of sulphuric acid, the aqueous solution is concentrated in the water-bath. Then are separated, in heat, crusts of rose-coloured crystals, chiefly consisting of sulphates of the cerium group. The mother-liquors of the crystals are saturated with neutral potassium sulphate, which occasions the precipitation of the rest of the cerium bases, carrying down with them a fraction of the yttrium bases. We isolate the latter by repeated precipitation of the sulphates with potassium sulphates, until the liquid floating above the crystalline deposit of double sulphates no longer contains earths precipitable by ammonia.

The yttrium earths are freed from alkali by repeated precipitation with ammonia, and subsequent washing. They are then converted into nitrates, after having been previously formed into oxalate.

The mean atomic weight of the metals of the yttrium earths thus isolated is between 105 and 106, if we do not include those which are mechanically carried down by the first precipitation of the double potassium sulphates, and which give a higher atomic weight, near 126.

The mixture of the nitrates (105 to 106) was submitted to fractionated decompositions at a temperature of 310° to 315°. The operation is effected on a cylindrical capsule of platinum, with a flat bottom, plunging into a bath of potassium and sodium nitrates in equal equivalents. The melted nitrate begins by giving off nitrous vapours, then it thickens, and is finally converted into a solid crystalline mass, solid at 310°. When all decomposition has ceased it is allowed to cool, and treated with hot water. The mass is separated into an insoluble sub-nitrate, representing about a fourth of the product employed, and a soluble portion of neutral nitrate. The latter is evaporated to dryness and submitted to the same treatment, and gives a further insoluble sub-nitrate and neutral nitrate. The sub-nitrates thus obtained are washed with hot water and transformed into sulphates, and we determine for each the corresponding atomic weight by ignition to bright redness, sufficiently prolonged.

We find (1) that the proportion of sub-nitrate separated diminished each time; (2) that the corresponding atomic weights decrease from 108 to 102, and then finally to 96, the lower limit, which has not yet been passed.

We have applied to the different fractions of the sub-nitrates obtained a second method of separation, founded upon the fractionated crystallisations of the sulphates. We evaporate the solution of the sulphates in the water-bath in a porcelain capsule, and separate the successive crystallisations which are formed.

We may concentrate the solution until the larger part of the product is deposited, isolate the relatively small part of the mother-liquid, and re-commence the same operation with the crystals. The atomic weight of the crystals obtained by the complete evaporation of these mother-liquors has for some time a value close upon 97 to 98, and then rises progressively.

Lastly, we have still made use of the method of frac-

tionated precipitation by ammonia, but only to check certain of our results.

By proceeding thus, and applying successively and alternately the procedure with the nitrate, and that with the sulphate, we have finally, and after many attempts, succeeded in isolating a colourless earth, the atomic weight of which is no longer appreciably modified either by fractionation with the nitrate, or with the sulphate, or by partial precipitation with ammonia. The fixed atomic weight at which we have arrived is very close upon 102 (101.95 and 102.4).

Can this earth be divided by other procedures? This is what ulterior researches must establish.

From the totality of our researches we believe that we may equally conclude that by following the same course we shall arrive at other fixed terms, above and below 102, and equally resisting the procedures of separation employed.—*Comptes Rendus*, cxii., p. 697.

ON NUMERICAL RELATIONS EXISTING BETWEEN THE ATOMIC WEIGHTS OF THE ELEMENTS.

By M. CAREY LEA.

IN the first part of a paper on the Ions it was shown that the elements were divisible into three great classes; those whose ions were always colourless, those whose ions were always coloured, and a smaller class whose ions were coloured at some valencies and colourless at others.*

It was also shown that the first class, those whose ions were always colourless, can be arranged in vertical lines so that the horizontal lines contained each a natural group. Also that the elements having both coloured and colourless ions were much more closely allied to these than to the group having always coloured ions. This last named class does not divide into groups at all, but forms series with the atomic weights immediately following one another.

Therefore as long as an element has any colourless ions it really seems to belong to the class with the ions all colourless. So much so that when the first class is tabulated the members of this transitional class find vacant spaces into which they naturally fall. To make this clear and to elucidate what follows I here reproduce Table II. from the first part in a condensed form.

I.	H 1	F 19	Cl 35.5	Br 80	J 127	—
II.	Li 7	Na 23	K 39	Rb 85	Cs 132	—
III.	—	—	Ca 40	Sr 88	Ba 137	—
IV.	—	—	Sc 44	Y 90	La 139	—
V.	—	—	Ti 48	—	—	—
VI.	—	—	V 51	Nb 94	Ta 183	—
I.	—	—	Mo 96	W 184	—	—
II.	—	—	Cu 63	Ag 108	Au 196	—
III.	Be 9	Mg 24	Zn 65	Cd 112	Hg 200	—
IV.	B 11	Al 27	Ga 69	In 114	Tl 204	—
V.	C 12	Si 28	Ge 72	Sn 118	Pb 206	Th 234
VI.	N 14	P 31	As 75	Sb 120	Bi 208	—
	O 16	S 32	Se 79	Te 125	—	—

In the case of some few elements it has not been easy to find published data sufficient to determine with absolute certainty the colour of the ions. Further study of this subject has led me to make a slight change in reprinting the above table. I had previously classed the metal cerium as transitional. The ceric ion is undoubtedly coloured, but as to the cerous iron there is some uncertainty. Its compounds are nearly colourless, but as they exhibit a slight red tinge the ions may perhaps be coloured. It therefore seems better in this uncertainty to place cerium alongside of the other members of its

group; it is therefore omitted from the above table. Also in the paper just referred to gold was placed amongst the elements having coloured ions only. The auric ion is certainly coloured, but about the aurous ion there is some doubt; the oxides and the haloids are coloured, but as they are insoluble they give no positive information. It appears, however, that when aurous chloride is dissolved in sodium chloride it yields a colourless solution from which colourless crystals are obtained. Various other double salts form both colourless solutions and colourless crystals. The following are examples:—Ammonium aurammonium sulphite, sodium aurothiosulphate, potassium aurocyanide, &c. ("Roscoe and Schorlemmer," 1st Ed., ii., pp. 380-1).

As it seems characteristic of the soluble salts to be colourless, I conclude that gold must be considered as having both coloured and colourless ions. It is therefore a transitional element and finds its place in the above table, where elements of that class appear in italics. It is, however, interesting to observe that just as these two metals cerium and gold are at the very limiting point between two classes, so there are spaces open for them in each of these classes, a circumstance that can hardly be fortuitous.

Table of Differences.

If the respective numbers of the first column in the preceding table be each subtracted from the corresponding number of the second column, the second column from the third, and so on, we obtain a series of differences which are given in the table below.

18	16.5	44.5	47
16	16	46	47
—	—	48	49
—	—	45	49
—	—	44	88
—	—	—	88
—	—	45	88
15	41.3	46.7	88
16	42	45	90
16	44	46	88
17	44	45	88
16	47	46	—

It has been remarked, I think as far back as the time of Dumas, that differences of 16 between the atomic weights frequently presented themselves, and occasionally differences of 45 or thereabouts. But these were scattered cases. In the above table of differences all the elements are represented with the exception of the comparatively small group having ions always coloured. As has been already said, this last group of elements, having nothing in common with other elements, cannot be classed with them, and will probably be found, when we know much more than we do now, to have a wholly different constitution.

There are several things worthy of remark in the above table. It will be seen that the differences at first approximate to 16. Then comes a long set of differences, twenty in number, beginning with 41.3, and gradually, but not regularly, increasing to 49. The remaining differences are all exactly 88, with one exception of 90; but as this is the difference between two metals of which comparatively little is known, and whose atomic weights cannot be considered as being accurately fixed (indium and thallium) it is quite probable that this exception may hereafter disappear.

It should be remarked that when the set of differences approximating 16 is once left behind, this difference does not reappear in a single case. The same is true of the differences averaging 45: this class of differences does not once reappear when 88 is reached.

For some time past it has been believed that the oxygen group does not end with tellurium, but contains still another member with a higher atomic weight. It will be observed that in both the above tables there remains a

* *American Journal of Science*, June, 1895. The second part will appear shortly.

Series of all the Elements in Numerical Order.

1 H	2 Li	3 Be	4 B	5 C	6 N	7 O	8 F	9 Ne	10 Na	11 Mg	12 Al	13 Si	14 P	15 S	16 Cl	17 Ar	18 K	19 Ca	20 Sc
9 Colorless																			
21 Ti	22 V	23 Cr	24 Mn	25 Fe	26 Co	27 Ni	28 Cu	29 Zn	30 Ga	31 Ge	32 As	33 Se	34 Br	35 Kr	36 Rb	37 Sr	38 Y	39 Zr	40 Nb
9 Colorless																			
41 Mo	42 Tc	43 Ru	44 Rh	45 Pd	46 Ag	47 Au	48 Hg	49 Tl	50 Pb	51 Bi	52 Po	53 At	54 Rn	55 Fr	56 Ra	57 Ac	58 Th	59 Pa	60 U
9 Colorless																			
61 Th	62 Pa	63 U	64 Np	65 Pu	66 Am	67 Cm	68 Bk	69 Cf	70 Es	71 Fm	72 Md	73 No	74 Lr	75 Ac	76 Th	77 Pa	78 U	79 Np	80 Pu
9 Colorless																			
81 Am	82 Cm	83 Bk	84 Cf	85 Es	86 Fm	87 Md	88 No	89 Lr	90 Ac	91 Th	92 Pa	93 U	94 Np	95 Pu	96 Am	97 Cm	98 Bk	99 Cf	100 Es
9 Colorless																			
101 Fm	102 Md	103 No	104 Lr	105 Ac	106 Th	107 Pa	108 U	109 Np	110 Pu	111 Am	112 Cm	113 Bk	114 Cf	115 Es	116 Fm	117 Md	118 No	119 Lr	120 Ac
9 Colorless																			
121 Th	122 Pa	123 U	124 Np	125 Pu	126 Am	127 Cm	128 Bk	129 Cf	130 Es	131 Fm	132 Md	133 No	134 Lr	135 Ac	136 Th	137 Pa	138 U	139 Np	140 Pu
9 Colorless																			
141 Am	142 Cm	143 Bk	144 Cf	145 Es	146 Fm	147 Md	148 No	149 Lr	150 Ac	151 Th	152 Pa	153 U	154 Np	155 Pu	156 Am	157 Cm	158 Bk	159 Cf	160 Es
9 Colorless																			
161 Fm	162 Md	163 No	164 Lr	165 Ac	166 Th	167 Pa	168 U	169 Np	170 Pu	171 Am	172 Cm	173 Bk	174 Cf	175 Es	176 Fm	177 Md	178 No	179 Lr	180 Ac
9 Colorless																			
181 Th	182 Pa	183 U	184 Np	185 Pu	186 Am	187 Cm	188 Bk	189 Cf	190 Es	191 Fm	192 Md	193 No	194 Lr	195 Ac	196 Th	197 Pa	198 U	199 Np	200 Pu
9 Colorless																			
201 Am	202 Cm	203 Bk	204 Cf	205 Es	206 Fm	207 Md	208 No	209 Lr	210 Ac	211 Th	212 Pa	213 U	214 Np	215 Pu	216 Am	217 Cm	218 Bk	219 Cf	220 Es
9 Colorless																			
221 Fm	222 Md	223 No	224 Lr	225 Ac	226 Th	227 Pa	228 U	229 Np	230 Pu	231 Am	232 Cm	233 Bk	234 Cf	235 Es	236 Fm	237 Md	238 No	239 Lr	240 Ac
9 Colorless																			
241 Th	242 Pa	243 U	244 Np	245 Pu	246 Am	247 Cm	248 Bk	249 Cf	250 Es	251 Fm	252 Md	253 No	254 Lr	255 Ac	256 Th	257 Pa	258 U	259 Np	260 Pu
9 Colorless																			
261 Am	262 Cm	263 Bk	264 Cf	265 Es	266 Fm	267 Md	268 No	269 Lr	270 Ac	271 Th	272 Pa	273 U	274 Np	275 Pu	276 Am	277 Cm	278 Bk	279 Cf	280 Es
9 Colorless																			
281 Fm	282 Md	283 No	284 Lr	285 Ac	286 Th	287 Pa	288 U	289 Np	290 Pu	291 Am	292 Cm	293 Bk	294 Cf	295 Es	296 Fm	297 Md	298 No	299 Lr	300 Ac
9 Colorless																			
301 Th	302 Pa	303 U	304 Np	305 Pu	306 Am	307 Cm	308 Bk	309 Cf	310 Es	311 Fm	312 Md	313 No	314 Lr	315 Ac	316 Th	317 Pa	318 U	319 Np	320 Pu
9 Colorless																			
321 Am	322 Cm	323 Bk	324 Cf	325 Es	326 Fm	327 Md	328 No	329 Lr	330 Ac	331 Th	332 Pa	333 U	334 Np	335 Pu	336 Am	337 Cm	338 Bk	339 Cf	340 Es
9 Colorless																			
341 Fm	342 Md	343 No	344 Lr	345 Ac	346 Th	347 Pa	348 U	349 Np	350 Pu	351 Am	352 Cm	353 Bk	354 Cf	355 Es	356 Fm	357 Md	358 No	359 Lr	360 Ac
9 Colorless																			
361 Th	362 Pa	363 U	364 Np	365 Pu	366 Am	367 Cm	368 Bk	369 Cf	370 Es	371 Fm	372 Md	373 No	374 Lr	375 Ac	376 Th	377 Pa	378 U	379 Np	380 Pu
9 Colorless																			
381 Am	382 Cm	383 Bk	384 Cf	385 Es	386 Fm	387 Md	388 No	389 Lr	390 Ac	391 Th	392 Pa	393 U	394 Np	395 Pu	396 Am	397 Cm	398 Bk	399 Cf	400 Es
9 Colorless																			
401 Fm	402 Md	403 No	404 Lr	405 Ac	406 Th	407 Pa	408 U	409 Np	410 Pu	411 Am	412 Cm	413 Bk	414 Cf	415 Es	416 Fm	417 Md	418 No	419 Lr	420 Ac
9 Colorless																			
421 Th	422 Pa	423 U	424 Np	425 Pu	426 Am	427 Cm	428 Bk	429 Cf	430 Es	431 Fm	432 Md	433 No	434 Lr	435 Ac	436 Th	437 Pa	438 U	439 Np	440 Pu
9 Colorless																			
441 Am	442 Cm	443 Bk	444 Cf	445 Es	446 Fm	447 Md	448 No	449 Lr	450 Ac	451 Th	452 Pa	453 U	454 Np	455 Pu	456 Am	457 Cm	458 Bk	459 Cf	460 Es
9 Colorless																			
461 Fm	462 Md	463 No	464 Lr	465 Ac	466 Th	467 Pa	468 U	469 Np	470 Pu	471 Am	472 Cm	473 Bk	474 Cf	475 Es	476 Fm	477 Md	478 No	479 Lr	480 Ac
9 Colorless																			
481 Th	482 Pa	483 U	484 Np	485 Pu	486 Am	487 Cm	488 Bk	489 Cf	490 Es	491 Fm	492 Md	493 No	494 Lr	495 Ac	496 Th	497 Pa	498 U	499 Np	500 Pu
9 Colorless																			
501 Am	502 Cm	503 Bk	504 Cf	505 Es	506 Fm	507 Md	508 No	509 Lr	510 Ac	511 Th	512 Pa	513 U	514 Np	515 Pu	516 Am	517 Cm	518 Bk	519 Cf	520 Es
9 Colorless																			
521 Fm	522 Md	523 No	524 Lr	525 Ac	526 Th	527 Pa	528 U	529 Np	530 Pu	531 Am	532 Cm	533 Bk	534 Cf	535 Es	536 Fm	537 Md	538 No	539 Lr	540 Ac
9 Colorless																			
541 Th	542 Pa	543 U	544 Np	545 Pu	546 Am	547 Cm	548 Bk	549 Cf	550 Es	551 Fm	552 Md	553 No	554 Lr	555 Ac	556 Th	557 Pa	558 U	559 Np	560 Pu
9 Colorless																			
561 Am	562 Cm	563 Bk	564 Cf	565 Es	566 Fm	567 Md	568 No	569 Lr	570 Ac	571 Th	572 Pa	573 U	574 Np	575 Pu	576 Am	577 Cm	578 Bk	579 Cf	580 Es
9 Colorless																			
581 Fm	582 Md	583 No	584 Lr	585 Ac	586 Th	587 Pa	588 U	589 Np	590 Pu	591 Am	592 Cm	593 Bk	594 Cf	595 Es	596 Fm	597 Md	598 No	599 Lr	600 Ac
9 Colorless																			
601 Th	602 Pa	603 U	604 Np	605 Pu	606 Am	607 Cm	608 Bk	609 Cf	610 Es	611 Fm	612 Md	613 No	614 Lr	615 Ac	616 Th	617 Pa	618 U	619 Np	620 Pu
9 Colorless																			
621 Am	622 Cm	623 Bk	624 Cf	625 Es	626 Fm	627 Md	628 No	629 Lr	630 Ac	631 Th	632 Pa	633 U	634 Np	635 Pu	636 Am	637 Cm	638 Bk	639 Cf	640 Es
9 Colorless																			
641 Fm	642 Md	643 No	644 Lr	645 Ac	646 Th	647 Pa	648 U	649 Np	650 Pu	651 Am	652 Cm	653 Bk	654 Cf	655 Es	656 Fm	657 Md	658 No	659 Lr	660 Ac
9 Colorless																			
661 Th	662 Pa	663 U	664 Np	665 Pu	666 Am	667 Cm	668 Bk	669 Cf	670 Es	671 Fm	672 Md	673 No	674 Lr	675 Ac	676 Th	677 Pa	678 U	679 Np	680 Pu
9 Colorless																			
681 Am	682 Cm	683 Bk	684 Cf	685 Es	686 Fm	687 Md	688 No	689 Lr	690 Ac	691 Th	692 Pa	693 U	694 Np	695 Pu	696 Am	697 Cm	698 Bk	699 Cf	700 Es
9 Colorless																			
701 Fm	702 Md	703 No	704 Lr	705 Ac	706 Th	707 Pa	708 U	709 Np	710 Pu	711 Am	712 Cm	713 Bk	714 Cf	715 Es	716 Fm	717 Md	718 No	719 Lr	720 Ac
9 Colorless																			
721 Th	722 Pa	723 U	724 Np	725 Pu	726 Am	727 Cm	728 Bk	729 Cf	730 Es	731 Fm	732 Md	733 No	734 Lr	735 Ac	736 Th	737 Pa	738 U	739 Np	740 Pu
9 Colorless																			
741 Am	742 Cm	743 Bk	744 Cf	745 Es	746 Fm	747 Md	748 No	749 Lr	750 Ac	751 Th	752 Pa	753 U	754 Np	755 Pu	756 Am	757 Cm	758 Bk	759 Cf	760 Es
9 Colorless																			
761 Fm	762 Md	763 No	764 Lr	765 Ac	766 Th	767 Pa	768 U	769 Np	770 Pu	771 Am	772 Cm	773 Bk	774 Cf	775 Es	776 Fm	777 Md	778 No	779 Lr	780 Ac
9 Colorless																			
781 Th	782 Pa	783 U	784 Np	785 Pu	786 Am	787 Cm	788 Bk	789 Cf	790 Es	791 Fm	792 Md	793 No	794 Lr	795 Ac	796 Th	797 Pa	798 U	799 Np	800 Pu
9 Colorless																			
801 Am	802 Cm	803 Bk	804 Cf	805 Es	806 Fm	807 Md	808 No	809 Lr	810 Ac	811 Th	812 Pa	813 U	814 Np	815 Pu	816 Am	817 Cm	818 Bk	819 Cf	820 Es
9 Colorless																			
821 Fm	822 Md	823 No	824 Lr	825 Ac	826 Th	827 Pa	828 U	829 Np	830 Pu	831 Am	832 Cm	833 Bk	834 Cf	835 Es	836 Fm	837 Md	838 No	839 Lr	840 Ac
9 Colorless																			
841 Th	842 Pa	843 U	844 Np	845 Pu	846 Am	847 Cm	848 Bk	849 Cf	850 Es	851 Fm	852 Md	853 No	854 Lr	855 Ac	856 Th	857 Pa	858 U	859 Np	860 Pu
9 Colorless																			
861 Am	862 Cm	863 Bk	864 Cf	865 Es	866 Fm	867 Md	868 No	869 Lr	870 Ac	871 Th	872 Pa	873 U	874 Np	875 Pu	876 Am	877 Cm	878 Bk	879 Cf	880 Es
9 Colorless																			
881 Fm	882 Md	883 No	884 Lr	885 Ac	886 Th	887 Pa	888 U	889 Np	890 Pu	891 Am	892 Cm	893 Bk	894 Cf	895 Es	896 Fm	897 Md	898 No	899 Lr	900 Ac
9 Colorless																			
901 Th	902 Pa	903 U	904 Np	905 Pu	906 Am	907 Cm	908 Bk	909 Cf	910 Es	911 Fm	912 Md	913 No	914 Lr	915 Ac	916 Th	917 Pa	918 U	919 Np	920 Pu
9 Colorless																			
921 Am	922 Cm	923 Bk	924 Cf	925 Es	926 Fm	927 Md	928 No	929 Lr	930 Ac	931 Th	932 Pa	933 U	934 Np	935 Pu	936 Am	937 Cm	938 Bk	939 Cf	940 Es
9 Colorless																			
941 Fm	942 Md	943 No	944 Lr	945 Ac	946 Th	947 Pa	948 U	949 Np	950 Pu	951 Am	952 Cm	953 Bk	954 Cf	955 Es	956 Fm	957 Md	958 No	959 Lr	960 Ac
9 Colorless																			
961 Th	962 Pa	963 U	964 Np	965 Pu	966 Am	967 Cm	968 Bk	969 Cf	970 Es	971 Fm	972 Md	973 No	974 Lr	975 Ac	976 Th	977 Pa	978 U	979 Np	980 Pu
9 Colorless																			
981 Am	982 Cm	983 Bk	984 Cf	985 Es	986 Fm	987 Md	988 No	989 Lr	990 Ac	991 Th	992 Pa	993 U	994 Np	995 Pu	996 Am	997 Cm	998 Bk	999 Cf	1000 Es
9 Colorless																			

space for such an element. Its atomic weight should exceed that of tellurium by the difference 88, and should therefore be 213. Finally, it may be said that the blanks in the table of differences are due to corresponding blanks in the table of atomic weights.

The change just mentioned in the classification of cerium and of gold makes a slight change in the table representing the whole range of elements in series. I therefore reproduce this table as corrected.

It will be observed that all the elements having only colourless ions appear on the base line. The elements having ions always coloured appear on the upper line parallel to the base line. The transition elements appear on the inclined lines.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 193).

CHAPTER XI.

CHEMICAL RESEARCHES ON THALLIUM, AND ITS TRI-OXIDE, HYDRATE, CHLORIDE, BROMIDE, IODIDE, NITRATE, CARBONATE, AND THALLOUS SULPHATE.

THE spectrum of thallium having been the subject of some discussion, I thought I ought to submit to a fresh examination the preparation and properties of the metal and its principal compounds. For this research I was fortunate in having put at my disposal:—1st, about 100 grms. of sulphate of thallium, prepared by the late M. Lamy during the course of his work on this metal; 2nd, some metallic thallium and carbonate of the same, through the kindness of Mr. Crookes, and prepared by himself. Lastly, I obtained some of the metal as prepared on a large scale in a chemical manufactory.

On the Sulphate of Thallium prepared by the late M. Lamy.—I started this research on sulphate prepared by the late M. Lamy. Having detected in it the presence of small quantities of sulphate of silver, of calcium, iron, sodium, and silicon, I had recourse to the following treatment to effect their separation:—

Pure ammonia was added to the boiling and saturated sulphate solution; it was kept boiling for several minutes in a large platinum dish, and then filtered. After the ferric hydrate was separated, the liquid was again treated with ammonia; kept boiling for several minutes, and filtered.

Traces of ferric hydrate being left a second time on the filter, I added ammonia a third time, and again boiled and filtered it.

After the iron was quite eliminated, I boiled the dilute solution, and added dissolved sesqui-carbonate of ammonium, little by little, to precipitate the calcium.

The slightly ammoniated liquid was filtered after cooling, to separate the carbonate of calcium mixed with a small quantity of crystallised thallosulphate.

I then evaporated to dryness the clear sulphate solution, to drive off the excess sesqui-carbonate of ammonium. The salt was dissolved in a saturated solution of sulphuric acid. The sulphuric solution was coloured brown.

When left alone in a platinum vessel under a bell-jar, it became violet-coloured, then quite colourless and clear, by depositing a slight deep red precipitate, consisting of sulphides of thallium and silver.

The clear liquid, when decanted, smelling strongly of sulphurous acid, was nevertheless added to a quarter of its volume of the sulphurous solution, and again left to itself in a closed vessel. After twenty-four hours it was quite colourless, and had no deposit.

A neutral solution of thallosulphate, from which the metals capable of being precipitated by sulphurous acid have been eliminated, is therefore not decomposed by this acid, contrary to the general opinion.

The deep red precipitate mentioned above, having been collected on a filter and washed with a saturated solution of sulphurous acid, was left to itself in damp air under a bell-jar. It was transformed by oxidation, chiefly into thallosulphate, and after washing left as residue a very small quantity of sulphide of silver.

The solution of the products of oxidation of the deep

red precipitate, when added to sulphurous acid and water, was neither coloured nor clouded after twenty-four hours in a closed vessel. This solution consisted entirely of neutral thallous sulphate, unchanged by a sulphurous acid solution. These facts prove that neutral thallous sulphate is only precipitated by sulphurous acid when it is associated with a metal capable of being thus transformed into an insoluble sulphide.

I evaporated the thallous sulphate solution to dryness in a platinum vessel, and heated the white residue to a dull red heat to destroy the small quantity of sulphate of ammonium, and make the silicic acid in it soluble.

The sulphate imparted the thallium colour to a hydrogen flame, and spectrum analysis of this flame immediately showed the sodium and thallium lines, *but no others*.

Four successive crystallisations were required before the spectrum of thallous sulphate could be seen without the sodium line. I did not conclude from this that there was no sodium present; I have enlarged upon this point elsewhere. When left in air under a bell-jar it showed the sodium line very strongly after a few days.

Crystallised thallous sulphate is colourless, and remains so even when exposed to direct sunlight in air.

I used this salt to prepare some of the pure metal, and also its trioxide and chloride.

I electrolysed an ammoniated solution of the sulphate in order to obtain at once the pure metal and its trioxide.

My reasons for using an ammoniated solution were as follows:—

When a saturated aqueous solution of sulphate in a platinum dish is subjected to electrolysis, it deposits thallium on the negative electrode in the platinum, and coats the positive electrode with hydrate or brown or black oxide. Mr. Crookes was the first to notice this fact. I found that, at the commencement of electrolysis, the ratio between the weight of thallium deposited in a metallic state and that deposited as an oxide is almost exactly as 2 to 1. This ratio quickly alters as sulphuric acid is liberated, and a time is reached when, at the negative electrode, hydrogen only is liberated, whilst the positive electrode is still being coated with black oxide. This action goes on with such regularity that when subjecting a solution of monothallic sulphate to a current, all the metal is eliminated in the form of hydrated trioxide.

Electrolysis of ammoniated sulphate, on the other hand, goes on quite uniformly. By maintaining a slight excess of ammonia in the liquid by successive additions, it deposits two parts by weight of metallic thallium to one part of thallium in the form of brown hydrate or black oxide, according to the temperature. By electrolysing ammoniated sulphate under a bell-jar full of *purified air*, thallium and its trioxide are produced, which, on spectrum analysis, fail to show the sodium line.

I made use of this last reaction to obtain directly the metal and its oxide, and to procure afresh from the oxide some sulphate and metallic thallium, by which means I could ascertain whether the sulphate, the metal, and the oxide contained a *spectroscopically identical base*.

I proceeded as follows:—Having kept part of the metal and the oxide produced, I transformed the rest of the metal, previously well washed with water, into sulphate, by attacking it with pure dilute sulphuric acid in a covered platinum vessel.

The oxide was also converted into the form of sulphate. For this purpose, after having treated it in succession with boiling water, then adding pure sulphuric acid and dilute ammonia, and finally washing it in pure water, the oxide was dissolved in a solution of sulphurous acid prepared in platinum, taking care to use an excess of acid and to keep the liquid boiling until it ceased to turn brown on the addition of ammonia,—that is to say, until the bisulphate of thallium, formed at first, was completely transformed into thallous sulphate by the excess of sulphurous acid and the action of heat. I found thus that brown

hydrate and black oxide, made by electrolysis of a sulphate, when previously treated with sulphuric acid, are soluble in an excess of a sulphurous solution, forming a perfectly clear liquid, which does not occur when the sulphate contains traces of *oxide of lead*, as it frequently does.

The sulphate solution made from the metal, and that made from oxide, had pure ammonia added to them, and were electrolysed, so as to precipitate oxide of thallium on a small dish, and metallic thallium on a sheet of platinum.

The metal and the oxide were, after being washed in boiling water, introduced into a hydrogen flame, and showed, on analysis, a thallium spectrum identical with that of the sulphate originally used, and with that of the metal and the oxide from which they were derived.

In order to be quite certain that I had made no mistake, I proceeded a third time to convert oxide into sulphate, and electrolyse the resulting sulphate. The spectrum of the metal and that of the oxide were identical. I concluded from this identity that the metal was chemically pure.

I re-converted the greater part of the metal and the oxide into sulphate by the methods above mentioned, and the latter into chloride. For this purpose a saturated aqueous solution of sulphate was added to water containing 10 per cent of pure liquid hydrochloric acid. The precipitate was washed with water containing 6 per cent of liquid hydrochloric acid, by means of a filter pump. I found it was necessary to add this amount of liquid acid to the water in order to dissolve as little chloride of thallium as possible. I continued to wash it with acidulated water until about half the precipitate was removed, without obtaining a liquid which would not cloud a solution of chloride of barium.

The precipitate therefore retained some sulphuric acid, probably in the form of thallous sulphate. The precipitate was quite white, and remained absolutely white after exposure to direct sunlight. Lamy has already noted that chloride of thallium is not altered by light. It has been stated, however, that exposure to light turns this compound greyish; I only met with this property in it when it was obtained by means of nitrate of thallium or thallous sulphate containing silver, and this is almost always the case when the salts are made from solutions which have not been treated with sulphuric acid.*

With the object of obtaining chloride of thallium free from sulphuric acid, I dissolved the precipitate in boiling water in a covered porcelain dish, and, after adding to the solution *one-sixth part* of its volume of liquid hydrochloric acid, I cooled it quickly. I repeated the solution and precipitation a second time, and obtained a granular chloride of thallium, perfectly white, *unaffected* by light, and quite free from sulphuric acid after washing it with pure water. Immediately after its preparation, or when kept under water in a *closed glass vessel*, it showed no signs of the presence of sodium. When left under a bell-jar full of dry air, it slowly occluded sodium, so that at the end of four or five days the sodium and thallium lines could both be seen. I do not conclude, from the absence of the sodium line in the chloride of thallium spectrum immediately after its production, that it did not contain a trace of sodium. I wish to make a reservation on this point, on which I shall enlarge later on.

Chloride of thallium, crystallised by cooling from a boiling solution, when stirred up with cold water, forms a liquid which is not clouded by the addition, in the cold, of concentrated hydrochloric acid.

Powdered chloride of thallium, obtained by precipitation in the cold from a solution of thallous sulphate or nitrate of thallium, by means of an excess of hydrochloric acid, when washed in succession with a 10 per cent solution of hydrochloric acid and with pure water, and

* Silver bearing chloride of thallium does not show the characteristic silver lines, whether the flame spectrum or the electric spectrum of this compound chloride be examined. The thallium line only is seen.

taken up by pure water, leaves after standing, a clear solution which is very greatly affected by the addition of concentrated hydrochloric acid.

Crystallised and powdered chlorides of thallium therefore behave, in the presence of hydrochloric acid, in a similar manner to granular and flocculent chlorides of silver.

The luminous spectrum of chloride of thallium is identical with that of the metal and its pure trioxide and sulphate.

(To be continued).

THE VOLUMETRIC COMPOSITION OF AMMONIUM CHLORIDE.

A CLASS AND LECTURE EXPERIMENT.

By D. CARNEGIE and H. WALES.

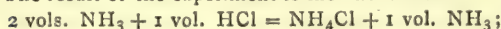
In an elementary course of chemistry, the fact that a certain volume of ammonia combines with an equal volume of hydrogen chloride to form ammonium chloride soon presents itself for statement and experimental verification. Given a mercury trough and a good supply of mercury, there would be no difficulty in executing the required experimental proof. But even in well-stocked laboratories, mercury in sufficient quantity for the performance of mercury-trough experiments by a class, is not always at hand, and considerations of portage often preclude the use of mercury by itinerant lecturers.

The following is a description of an experimental proof of the volumetric composition of ammonium chloride which does not involve the use of mercury. It is founded on the fact that kerosene is very readily saturated by ammonia.

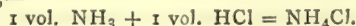
In the accompanying figure *a b* represents a glass tube of about 2 c.m. diameter and 55 c.m. length. At its upper end it is provided with a ground glass stopper, *s*, and at one-third of its length from this end is a wide-bored stopcock, *s'*. The capacity of the portion *b* of the tube, from *s'* down to a fiducial mark coincident with the level of the liquid in *c*, is exactly twice that of the portion *a*.

By downward displacement *a* is filled with hydrogen chloride at the temperature and pressure of the air in the room. The portion *b* is then filled with kerosene which has been saturated with dry ammonia, and the tube is inverted in the small glass trough *c*, which also contains ammoniated kerosene. Dry ammonia at the temperature of the room is now passed into *b*, till the kerosene stands at the fiducial mark both inside and outside the tube. On now opening the stopcock, *s'*, the gases combine, and after time has been allowed for the radiation of the heat of combination the kerosene rises to the level of the stopcock, while the portion *a* of the tube, now densely coated with a white deposit of NH_4Cl , remains filled with the excess of ammonia.

The result of the experiment is then as follows:—



or, subtracting 1 vol. NH_3 from both sides of the equation,—

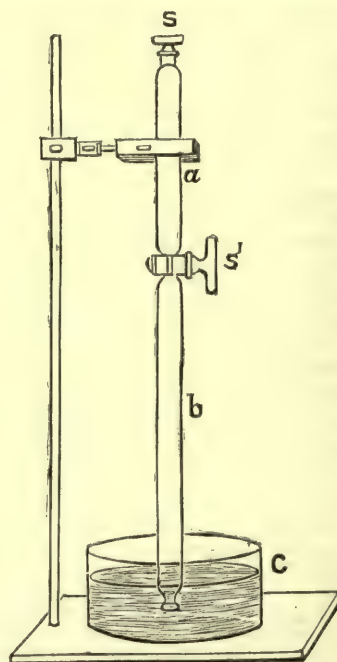


The following question may suggest itself:—Why not make *b* of the same volume as *a*, so as to get a "complete vacuum" on the combination of the gases, and therefore a complete filling of the tube with ammoniated kerosene?

The answer is to the effect that this was in fact the procedure which we at first adopted; but we found that under these conditions, the kerosene does not completely fill the tube after combination of the gases, the reason being that the ammoniated kerosene gives off its ammonia to the vacuum. This evolution of ammonia from the ammoniated kerosene does not take place to any appreci-

able extent under the partial pressure (nearly atmospheric pressure) which obtains in the case of a tube proportioned as in the figure.

We may add that the volume composition of NH_4Cl may be proved by the method described to a much higher degree of accuracy than can the statement, met with in many books on chemistry, to the effect that mercury rises



and fills a eudiometer in which electrolytic gas has been exploded. In this connection it is interesting to refer to E. W. Morley's recent paper on the combining volumes of hydrogen and oxygen. In this paper he states that he has not yet definitely determined the conditions of voltage, temperature, and dilution of acid, under which electrolytic gas has exactly the composition expressed in the symbolism $2\text{H}_2 + \text{O}_2$.

The Leys School, Cambridge.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

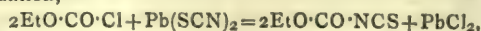
Ordinary Meeting, March 19th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 162).

44. "The Action of Lead Thiocyanate on the Chlorocarbonic Esters. Part I. Carboxyethylthiocarbimide and its Derivatives." By ROBERT E. DORAN.

In July, 1895, the existence of di-acidylthiocarbimides in solution was shown by Dixon and Doran (*Trans.*, lxxvii., 565), and the present communication contains an account of the preparation of a more highly oxidised thiocarbimide. Interaction occurs between lead thiocyanate and ethyl chlorocarbonate in accordance with the equation,—



and the product was obtained by distillation under diminished pressure as a colourless highly refractive liquid, possessing a pungent fungus-like odour and the

general properties of a thiocarbimide. The following derivatives were prepared and examined:—

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5$, ab-*Carboxyethylphenylthiocarbimide*. From the thiocarbimide and aniline; pure white, apparently monoclinic tables, m. p. 130°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5 \cdot CH_3$, ab-*carboxyethylbenzylthiocarbimide*. By interaction with benzylaniline; colourless needles, m. p. 106·5—107·5°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5 \cdot CH_3$, ab-*carboxyethyl-orthotolylthiocarbimide*. By interaction with o-toluidine; long white prisms, m. p. 152·5°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5 \cdot CH_3$, ab-*carboxyethyl-paratolylthiocarbimide*. By interaction with p-toluidine; white, glistening, flattened prisms, m. p. 148—149°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_{10}H_7$, ab-*carboxyethyl-α-naphthylthiocarbimide*. By interaction with α-naphthylamine; granular prisms, m. p. 183—183·5°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_{10}H_7$, ab-*carboxyethyl-β-naphthylthiocarbimide*. Faintly pink plates, having a pearly lustre, m. p. 155—155·5°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5 \cdot (CH_3)_2$, ab-*carboxyethyl-metoxylthiocarbimide*. By interaction with m-xylidine; pearly lozenges, m. p. 152·5—153°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5 \cdot OH$, ab-*carboxyethyl-p-hydroxyphenylthiocarbimide*. By interaction with p-aminophenol; oblique rhombic prisms, m. p. 198·5—199°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot CH_3$, ab-*carboxyethylmethylthiocarbimide*. By interaction with methylamine; long prisms, m. p. 119—120°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_2H_5$, ab-*carboxyethylethylthiocarbimide*. By interaction with ethylamine; fine oblique prisms, m. p. 79—80°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_4H_9$, ab-*carboxyethylisobutylthiocarbimide*. By interaction with isobutylamine; feathery tufts of needles, m. p. 53—54°.

$C_2H_5O \cdot CO \cdot N : C : NH_2 \cdot SH$, *carboxyethylthiourea*. By interaction with ammonia; long prisms, m. p. 139—140°.

$C_2H_5O \cdot CO \cdot N : C : NH \cdot C_6H_5 \cdot CH_2 \cdot (SH)$, *carboxyethylphenylbenzylthiourea*. By interaction with benzylaniline; long needles, m. p. 93—94°.

$C_2H_5O \cdot CO \cdot N : C : NH \cdot C_5H_{10} \cdot SH$, *carboxyethylpiperidylthiocarbimide*. By interaction with piperidine; fine interlaced needles, m. p. 99—99·5°.

$C_2H_5O \cdot CO \cdot NH \cdot C \begin{smallmatrix} \diagup N \cdot NH \cdot C_6H_5 \\ \diagdown SH \end{smallmatrix}$, *carboxyethylphenyl-semithiocarbimide*. By interaction with phenylhydrazine; fine white needles, m. p. 146·5°.

The five following esters of thiocarbamic acid were obtained by treating the corresponding alcohols with the thiocarbimide:—

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OCH_3$, *methyl carboxyethylthiocarbamate*. Feathery tufts of needles, m. p. 65—66°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OC_2H_5$, *ethyl carboxyethylthiocarbamate* (carboxyethyl-β-thiourethane). Rosettes of faintly yellow needles, m. p. 44—45°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OC_3H_7$, *propyl carboxyethylthiocarbamate*. Thick yellow prisms, m. p. 31—32°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OC_4H_9$, *isobutyl carboxyethylthiocarbamate*. A pale greenish yellow liquid, which did not solidify at -8°.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OC_6H_5 \cdot CH_2$, *benzyl carboxyethylthiocarbamate*. Tufts of white needles, m. p. 66—67°.

In the course of this investigation it is shown that the three following substances, "ethylic thioaleophanate" (Peitzsch, *Berichte*, vii., 896), "ethylic phenylthioaleophanate" and "ethylic isophenylthioaleophanate" (Seidel, *Journ. Prakt. Chem.*, [2], xxxii., 261) have been incorrectly named. The first mentioned appears to be a pseudothiourea; the second an unstable equimolecular combination of ethyl chlorocarbonate and phenylthiocarbamide; whilst the third is identical with the symmetrical carboxyethylphenylthiocarbamide obtained by the writer.

45. "An Auxiliary Assay Balance." By ROBERT LAW, F.I.C.

This paper describes a new form of balance applied to

bullion assaying, the object of which is to give the weight of the gold "cornet" with sufficient accuracy to enable the assayer to put the correct weight in the pan of the ordinary assay balance, and to decide the remaining fractions by means of the rider alone. This auxiliary balance is of such dimensions as to be easily accommodated in the case of the ordinary assay balance. The advantages claimed are—

1. Saving of time in weighing when gold of varying finenesses is under assay.
2. Reduction of the wear in the weights.
3. Increased life for the ordinary assay balance.
4. Avoidance of much of the concentrated attention which tends to make the assayer's work monotonous.

46. "Charas: the Resin of Indian Hemp." By T. B. WOOD, M.A., W. T. N. SPIVEY, M.A., B.Sc., and T. H. EASTERFIELD, M.A., Ph.D.

The authors have examined "charas," the exuded resin of *Cannabis indica*, with a view to the isolation of the active principle. The method adopted consisted in the fractional distillation of the ethereal extract prepared from the crude substance. By this means four compounds were isolated:—(1) A terpene, b. p. 170—180°. (2) A sesquiterpene, b. p. 258—259°, identical with that previously obtained by Valenta from Personne's "cannabene," the green oil obtained when the hemp plant is distilled with water. (3) A paraffin, probably $C_{29}H_{60}$, m. p. 63·5—64°. (4) A red oil, formula $C_{18}H_{24}O_2$, semi-solid below 60°, and boiling constantly at 265° at 20 m.m. pressure; this compound is present to the extent of 33 per cent in the sample of charas examined. In doses of 0·05 gm. it produces intoxication, followed by sleep. The substance has also been isolated by the authors from a number of pharmaceutical preparations made from the plant. The resin as prepared by T. and H. Smith in 1847 contains no less than 80 per cent of the oil. There can be no doubt that the characteristic action of Indian hemp is due to the presence of this compound, the constitution of which is under investigation.

47. "Note on the Decomposition of α-Chloronitrocammphor." By ARTHUR LAPWORTH, D.Sc.

It has long been known that α-bromo- and α-chloronitrocammphor undergo, when heated, a somewhat violent decomposition, resulting in the liberation of nitrous fumes and free halogen and the formation of products of unknown composition. The author has examined the residual mixtures, and has succeeded in obtaining, by the decomposition of α-chloronitrocammphor, some quantity of a yellow substance, which crystallises in long needles melting at 196—198°, volatilises slightly at the ordinary temperature, and yields a hydrazone melting at 169—171°.

This substance proves to be identical with the camphorquinone obtained by Claisen (*Ber.*, xxii., 530) from isonitroso-cammphor. Found, C=72·1; H=8·6. Required for $C_{10}H_{14}O_2$, C=72·3; H=8·4 per cent.

48. "π-Bromocammphor." By C. REVIS, Assoc. C.G. Inst., and F. STANLEY KIPPING, Ph.D., D.Sc.

The dextrorotatory π-monobromocammphor which was first obtained by heating camphorsulphonic bromide (Kipping and Pope, *Trans.*, lxvii., 1895, 371), can be more conveniently prepared from απ-dibromocammphor (*loc. cit.*). The last-named substance is readily attacked in alcoholic solution by sodium amalgam, and, under suitable conditions, the α-halogen atom only is displaced by hydrogen with formation of π-bromocammphor; the substitution of hydrogen for the α-halogen atom may also be accomplished with the aid of zinc-dust and acetic acid. The yield of the π-bromocammphor is good in both cases, but other products are also formed; the odour of camphor is very noticeable when reduction has proceeded for some time, and a crystalline substance melting at 248° has been isolated in small quantities.

This by-product does not contain bromine, and its formation appears to be the result of condensation, an analysis having given results which point to the formula

$C_{20}H_{30}O_2$. It crystallises in colourless hemimorphic prisms from dilute alcohol, and is readily soluble in chloroform, benzene, and acetic acid.

As π -bromocamphor is now obtainable in large quantities without much difficulty, its derivatives are being investigated. It is easily converted into a crystalline *oxime*, which melts at 124.5° . This oxime crystallises from dilute alcohol in colourless needles, and is readily soluble in chloroform, ethylic acetate, benzene, &c.

The study of the oxime is of particular interest, because if its chemical behaviour should prove to be analogous to that of camphoroxime—as seems to be the case—it will be possible to discuss the structural formulæ for the campholenic acids from a totally new point of view.

49. "*Oxidation Products of α -Bromocamphorsulphonic Acid.*" By ARTHUR LAPWORTH, D.Sc., and F. STANLEY KIPPING, Ph.D., D.Sc.

In the hope of obtaining a new series of oxidation products from camphor, the authors have commenced the examination of the compounds which are formed on boiling moderately concentrated nitric acid with ammonium α -bromocamphorsulphonate.

After heating during many hours, the nitric acid solution contains a small quantity of a substance which is almost insoluble in water, and is deposited in crystals on cooling and diluting. This compound separates from acetic acid in fine orthorhombic prisms. It melts at $188-189^\circ$, and is insoluble in cold dilute sodium carbonate solution; it appears to be a *sulpholactone* derived from a hydroxydibromocamphorsulphonic acid by the elimination of one molecular proportion of water. Found, $C=31.4$, $H=2.96$, $Br=41.3$, $S=8.5$ per cent. $C_{11}H_{12}SO_4Br_2$ requires $C=30.9$, $H=3.09$; $Br=41.2$, $S=8.2$ per cent.

The acid filtrate from this crystalline substance contains sulphuric acid, but in quantities which show that only a very partial elimination of the sulphonic group has occurred during the oxidation. After removing the sulphuric acid and repeatedly evaporating the filtered solution until almost free from nitric acid, there remains a thick acid syrup, from which it is very difficult to isolate the several constituents; this is owing to the fact that the product consists of hygroscopic sulphonic acids which do not lend themselves to the ordinary processes of extraction, distillation, precipitation, &c.

As the result of a number of operations, however, two crystalline substances have so far been obtained from this mixture. One of these is a sulphonic acid which crystallises from a mixture of methyl alcohol and ethylic acetate in pyramidal forms, and melts at about $156-158^\circ$, with evolution of gas; this compound is very readily soluble in water, from which it separates in hydrated crystals melting at $128-133^\circ$. Analysis of the anhydrous substance gave results agreeing with those required for a *hydroxydibromocamphorsulphonic acid*. (Found, $C=29.9$, $H=3.8$, $Br=38.4$, $S=8.1$ per cent. Calculated for $C_{10}H_{14}SO_3Br_2$, $C=29.5$, $H=3.5$, $Br=39.4$, $S=7.9$ per cent). The other compound isolated from the mixture is apparently the ammonium dihydrogen salt of a π -sulphocamphoric acid. (Found, $C=40.2$, $H=6.4$ per cent. Calculated for $C_{10}H_{15}O_4SO_2ONH_4$, $C=40.4$, $H=6.4$ per cent), but it requires further analysis; it separates from alcoholic ethyl acetate in microscopic plates, and is extremely soluble in water, but nearly insoluble in cold acetone.

When the crude syrupy oxidation product is freed from water as much as possible, and then treated with phosphorus pentabromide, it yields a considerable proportion of products, which are nearly insoluble in water; from these it is easy to isolate a compound which crystallises from acetone in lustrous prisms, and decomposes at about 191° with effervescence; this substance is insoluble in cold dilute sodium carbonate solution, and only sparingly soluble in most of the ordinary organic solvents; it seems to be a *sulphonic bromide* derived from hydroxydibromocamphorsulphonic acid.

The formation of the dibromo-derivatives described in this note must be partly attributed to the action of the bromine which is liberated during the oxidation of some of the bromocamphorsulphonic acid to sulphocamphoric acid.

50. "*On the Xylic and Xylidinic Acids.*" By WILLIAM HENRY BENTLEY and WILLIAM HENRY PERKIN, jun.

The oxidation of pseudocumene by dilute nitric acid was first carried out by Fittig and Laubinger (*Annalen*, cli., 257), who, by this means, obtained xylic and paraxylic acids, methyl terephthalic acid, and some nitro-compounds.

The authors have found that in addition a small quantity of *methyl isophthalic acid*,—

$CH_3 \cdot C_6H_3(COOH)_2$ [$CH_3 : COOH : COOH = 1 : 2 : 4$], is produced, which is separated from its isomeride by the fractional crystallisation of the methylic salts.

Methylic methylterephthalate crystallises from the methylic alcohol in needles melting at $58-60^\circ$, while methylic methylisophthalate separates in needles melting at 73° .

The reduction products of all four acids are being studied in order to compare their properties with those of some acids obtained from camphoric acid.

Paraxylic acid,—

$(CH_3)_2 \cdot C_6H_3 \cdot COOH$ [$CH_3 : CH_3 : COOH = 1 : 2 : 4$], when reduced with sodium and amyl alcohol yields a mixture of tetra- and hexa-hydroparaxylic acid.

Tetrahydroparaxylic acid, $C_8H_{13}COOH$, crystallises from light petroleum in prisms melting at 83° , and readily absorbs bromine forming a dibrom-acid, $C_8H_{13}Br_2COOH$, which melts at $121-123^\circ$.

Hexahydroparaxylic acid, $C_8H_{15}COOH$, is an oil with a disagreeable smell, boiling at 251° under a pressure of 748 m.m.

Ethylic hexahydroparaxylic acid, $C_8H_{15}COOC_2H_5$, is a pleasant smelling oil boiling at 224° (758 m.m.). The anilide of hexahydroparaxylic acid, $C_8H_{15}CO \cdot NH \cdot C_6H_5$, separates from light petroleum in prisms melting at $113-115^\circ$.

Hexahydroparaxylic chloride, $C_8H_{15}CO \cdot Cl$, is a liquid having a disagreeable odour, boiling at 110° (25 m.m.).

Ethylic bromhexahydroparaxylic acid, $C_8H_{14}BrCOOC_2H_5$, is a heavy liquid, boiling at $170-180^\circ$ (60 m.m.).

PHYSICAL SOCIETY.

Ordinary Meeting, April 24th, 1896.

Captain W. DE W. ABNEY, President, in the Chair.

A PAPER by Mr. R. A. LEHFELDT on "*Symbolism in Thermodynamics*" was, in the absence of the author, read by the Secretary.

The author proposes a system of about twenty-four separate symbols for the different quantities in thermodynamics.

Prof. SILVANUS THOMPSON said he was not at all favourably impressed by the symbols proposed. In particular, it was becoming usual to restrict the use of Greek letters to the representation of specific quantities or angles, and the author's proposal seemed in this way a retrograde step.

Prof. PERRY said he did not care for the suggested symbols.

Mr. ELDER thought the author's system would be a very severe tax on the memory, for he did not make use of suffixes, which can be made in a great measure to define the symbol to which they are attached.

Mr. APLEYARD read a paper on "*The Adjustment of the Kelvin Bridge.*"

In a recent paper read before the Society, Mr. Reeves had described a modified form of Kelvin bridge in which a double adjustment was necessary. The author proposes

to employ two wires stretched side by side, with a sliding contact in connection with the galvanometer on each. These contacts are rigidly connected together, so that the segments into which one wire is divided necessarily bear to one another the same ratio as do the segments of the other wire. Hence a single adjustment is sufficient to give balance.

Mr. REEVES said that apparently the author had completely missed the object of his (the speaker's) paper. For the object there aimed at was to make use of such sets of resistance coils as are always to be found in any laboratory. In the author's arrangement it would be necessary to carefully calibrate the two wires, and also, since the resistances used must necessarily be small, to determine the resistance of the contacts.

Prof. AYRTON (communicated) said the author's suggestion was ingenious, but did not obviate the necessity for much of Mr. Reeves's "addition." Further, Mr. Reeves's proposal to employ ordinary resistance boxes was not made because such resistances are absolutely necessary, but because since they are to be found in every laboratory, their use saves the expense of such a wire resistance, accurately calibrated, as Mr. Appleyard employed.

Mr. APPELYARD, in his reply, said that his instrument was designed for use in a factory, where the time saved in making a series of tests was of more importance than the cost of the instrument.

Mr. J. FRITH read a paper on "*The Effect of Wave-Form on the Alternate Current Arc.*"

The author finds that an arc has the power of modifying the wave-form in a circuit in which it is included. Thus, in the case of a dynamo for which, on open circuit, the curve of E.M.F. was decidedly peaked, it was found that when this dynamo was employed to feed an arc that the curve became changed to a flat-topped form. It is interesting to remember that the candle-power of the arc is greater when the wave-form is flat-topped than when it is peaked. By altering the resistance in series with the arc, it is possible to alter the character of the curve; for, as the resistance in series with the arc increases, the arc affects the wave-form less and less. In some recent experiments described by Dr. Fleming, a resistance of about 7 ohms was used in series with the arc, so that the wave-form of the generator, which is not an efficient form, was forced on the arc. In practice, however, where a resistance is not used in series with the arc this is not the case, and the differences between the efficiency obtained for alternate current arcs in the laboratory and that claimed in practice may thus be accounted for.

Mr. BLAKESLEY said it seemed as if the more nearly the alternate current resembles a direct current, and the longer in each period the current remains constant, the greater is the efficiency of the arc.

Mr. PRICE asked what was the cause of the reaction of the arc on the wave-form?

Mr. TREMLETT CARTER asked whether previous observers' results were vitiated by this action of the arc on the wave-form?

Prof. AYRTON (communicated) considered the author's suggestion of great importance, as bearing on the efficiency of the alternate current arc.

Prof. S. P. THOMPSON said that the dynamo employed by the author was one in which there was a large quantity of iron in the armature, so that the self-induction was large. Was it not on account of this large coefficient of self-induction, which would tend to keep the current constant, that the arc was able to alter the wave-curve? If an arc is connected to the mains of a supply station in which a number of machines in parallel are feeding a number of lamps, would the arc still be able to affect the wave-form of the current?

Mr. TREMLETT CARTER asked if the author had tried the effect of replacing the arc by a resistance such that it would absorb the same volts as did the arc, and comparing

the curves for the current and impressed P.D. with those obtained with the arc.

The AUTHOR, in his reply, said that the effect of the self-induction of the machine was shown in the curves. Current curves had not been taken with the arc straight on the machine. The current and self-induction were the same for all the curves, the voltage of the machine being increased by increasing the field when resistance was placed in series with the arc. When, as is commonly the case, special machines are used to supply arcs, and the load consists solely of arcs, the arcs could alter the character of the wave form. If the arc is replaced by a resistance, the wave form is of the same type as is obtained for the E.M.F. of the machine on open circuit.

The Society then adjourned till May 8th.

NOTICES OF BOOKS.

Chemical Novelties, New Laboratory Appliances, New Methods of Researches applied to Science and to Industry. ("Les Nouveautés Chimiques, Nouveaux Appareils de Laboratoire, Méthodes Nouvelles de Recherches appliquées à la Science et à l'Industrie.") By CAMILLE POULENC, D.Sc. Paris: J. B. Baillière and Son; Pouleuc Frères. 8vo., pp. 136.

THIS profusely illustrated work is devoted to the description of new and improved laboratory apparatus. Among these may be especially mentioned Mercier's new ureometer, Bernard's calcimeter, Moissan's apparatus for the determination of boron, Bourlier's arrangement for the determination of plaster in wine, Nevière and Hubert's instrument for the recognition of fluorine in wines, and Procter's tintometer and colorimeter—a modification of the well-known instrument of Lovibond. There is also a description and figure of M. Thiery's comparative hemaspectroscope, by means of which it is said that 1 part of blood may be detected in 850,000 parts of any liquid.

There is also an account of Schlumberger's "aseptic filter," which is said to effect a perfect sterilisation not merely of ordinary river waters, but even of sewage. The ordinary filtering materials are coated with aluminium benzoate and manganic carbon.

Fruit and Gardens for the People. By the Hon. DUDLEY CAMPBELL. A Preface to the "Case against Butchers' Meat," by CHARLES W. FORWARD. London: Bennett and Russell, Ltd. 1896.

THIS pamphlet, as appears from its second title, is a vegetarian manifesto, and as such lies distinctly outside the jurisdiction of the CHEMICAL NEWS.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 13, March 30, 1896.

Different Properties of the Invisible Radiations emitted by the Salts of Uranium, and of the Radiation of the Antikathodic Wall of a Crookes Tube.—Henri Becquerel.—Inserted in full.

Penetration of Gases into the Glass Walls of Crookes Tubes.—M. Gouy.—Already inserted.

Use of Heteroform Magnetic Fields in Photography by the X Rays.—Georges Meslin.—Already inserted.

Time of Exposure in Photographs by the X Rays.—James Chappuis.—Will be inserted in full.

Action of the X Rays upon Electrified Bodies.—L. Benoist and D. Hurmuzescu.—Will be inserted in full.

Refraction of Röntgen's Rays.—F. Beauland.

Diffraction and Polarisation of Röntgen's Rays.—G. Sagnac.—(See p. 201).

Stereoscopic Photographs obtained with the X Rays.—A. Imbert and H. Bertin-Sans.—The authors describe the arrangement which they have employed for surgical purposes in detecting the position of a foreign body within human tissues.

Determination of the Depth or the Position of a Foreign Body in the Tissues by means of the X Rays.—Abel Buguet and Albert Gascard.—Further surgical applications of the Röntgen rays.

Action of the X Rays upon a Phycomyces.—L. Errera.—It appears from the author's experiments, conducted at the Solvay Institute of the University of Brussels, that the phycomyces is not sensitive to the Röntgen rays.

On the Röntgen Rays.—Charles Henry.—This paper will be inserted as early as possible.

Reply to some Observations of Henri Becquerel on a Paper "On the Principle of an Accumulator of Light."—Charles Henry.

Observations relating to Charles Henry's Reply.—Henri Becquerel.

Safrol and Isosafrol. Synthesis of Isosafrol.—Ch. Moreu.—The synthesis of isosafrol, setting out from methylene-homocafeic acid, establishes its constitution in an indisputable manner; it shows that this compound is certainly propenylmethylene-pyrocatechine. If we proceed by the method of exclusion safrol will be allylmethylene-pyrocatechine.

On Citronellol and its Isomery with Rhodinol.—Ph. Barbier and L. Bouveault.—Rhodinol is distinct from citronellol since the corresponding acids are distinct.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., Nos. 119 and 120.

These issues contain no chemical matter.

MEETINGS FOR THE WEEK.

- MONDAY, 4th.—Society of Arts, 8. (Cantor Lectures). "Applied Electro-Chemistry," by James Swirburne.
— Society of Chemical Industry, 8. "Reproduction of Colour by Photography," by E. J. Wall. "Artificial Silk," by Messrs. Cross and Bevan.
- TUESDAY, 5th.—Royal Institution, 3. "Ripples in Air and on Water," by C. V. Boys, F.R.S.
— Society of Arts, 8. "Australia's Prospects in British Markets," by James F. Dowling.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
- WEDNESDAY, 6th.—Society of Arts, 8. "High Explosives and Smokeless Powders," by Hudson Maxim.
— Society of Public Analysts, 8. "The Composition of Human Fat," by C. A. Mitchell, B.A.
— "Note on an Incrustation found in Hot-water Pipes," by J. Augustus Voelcker, M.A., B.Sc., Ph.D.
— "The Examination of Commercial Milk Sugar," by H. Droop Richmond.
— "Note on 'Drawn' or Exhausted Caraways," by Bernard Dyer, D.Sc., and J. F. H. Gilbard.
- THURSDAY, 7th.—Royal, 4.30.
— Royal Institution, 3. "The Art of Working Metals in Japan," by W. Gowland, F.C.S.
— Chemical, 8. "Ballot for Election of Fellows.
- FRIDAY, 8th.—Royal Institution, 9. Electric Shadows and Luminescence," by Prof. Silvanus P. Thompson, F.R.S.
— Astronomical, 8.
— Physical, 5.
- SATURDAY, 2nd.—Royal Institution, 3. "Three Emotional Composers—J. Berlioz," by F. Corder, Curator, Royal Academy of Music.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1902.

ON THE MECHANICAL ACTION EMANATING FROM CROOKES TUBES.

By A. FONTANA and A. UMANI.

In the *Comptes Rendus* for March 23rd there was published a paper by J. R. Rydberg "On Mechanical Action emanating from Crookes Tubes." We must make known that we have developed this subject in a memoir published in the *Rendiconti della R. Accademia dei Lincei* (vol. v., March 1, 1896), entitled "Azione del Tubo di Crookes sul Radiometro."

We have observed the facts described by Gossart and Chevalier (*Comptes Rendus*, Feb. 10, 1896), but, contrary to the conclusions of these authors, we have found that the mechanical action is due to charges of statical electricity, and not to the rays of Röntgen.

We have reproduced these facts without the intervention of a Crookes tube, with the aid of a Leyden jar. On the other hand, we have pointed out that the mechanical action upon the wings fades away when we shut up the Crookes tube, and the coil or the radiometer, in a metallic chest placed in communication with the earth.

We have also studied the action of various diaphragms, and observed that the permeability, greater or smaller for the X rays, has no influence on the directive force of the tube, and, on the contrary, that diaphragms which are good conductors of electricity in connection arrest the mechanical action, whilst dielectrics do not arrest it.

We believe, therefore, that we have been the first to exclude all relation between the rays of Röntgen and the phenomena observed with the Crookes tube, and to deny the accuracy of the method proposed for measuring the intensity of the X rays.—*Comptes Rendus*, cxxii., p. 840.

APPLICATION OF PHOTOGRAPHY BY RÖNTGEN RAYS TO ANALYTICAL RESEARCHES ON VEGETABLE MATTER.

By FERNAND RANVEZ.

PHOTOGRAPHY by means of the X rays can render precious services in analytical research, and especially in the analysis of vegetable articles of food, where it will detect certain of the most frequent falsifications—those effected by the addition of mineral substances.

This method offers manifold advantages: it requires only small quantities of the substances; it leaves the specimens completely intact; it allows us to effect in a very short time a great number of examinations (about a quarter of an hour sufficing for a series of specimens). Lastly, the proof obtained is a piece of convictive evidence quite demonstrative, easily understood even by persons strange to any analytical operation.

The experiments which I have made refer to three samples of falsified saffron, taken in trade. These products consisted of mixtures in different proportions of pure saffron and saffron coated with barium sulphate. The filaments of the latter were found surrounded with a shell of mineral matter. The adulteration was very skilfully masked, and could not be suspected on a mere inspection of the merchandise.

I arranged on one and the same sensitive plate, enclosed in black paper, quantities of the three adulterated samples

almost equal. No. II. contains 62.13 per cent of mineral matters, No. III. 28.69 per cent, No. IV. 22.21 per cent, and along with them a specimen of pure saffron. The whole was submitted for three minutes to the influence of the rays emanating from a Crookes tube.

The pure allowed itself to be traversed by the X rays, and produced on the proof merely shadows scarcely visible, not acting, so to say, upon the paper of the positive proofs. The three falsified samples acted strongly upon the sensitive plate, marking very distinctly the filaments coated with barium sulphate, whilst the stigmata of the pure product, which were mixed with it, appeared only as scarcely perceptible shadows analogous to those of the former product.

The photographic proofs which accompany this note show the distinctness of the results obtained, and enable us to foresee the services which this method will render in its future applications.—*Comptes Rendus*, cxxii., p. 841.

ACTION OF THE X RAYS UPON ELECTRISED BODIES.

By L. BENOIST and D. HURMUZESCU.

SINCE our first communication on the X rays (February 3), in which we announced that these rays have the property of completely discharging electrised bodies without causing new electrification to appear, and in which we founded upon this property an actinometric method applicable to these radiations, there have been published several memoirs relating to the same phenomena. That of J. J. Thomson formulates conclusions entirely in agreement with our own. The others, such as that of A. Righi, that of Borgmann and Gerchun, and that of H. Dufour, whilst agreeing as concerns the discharge of electrised bodies, whatever is the sign of their electrification, signalise an electrification produced directly by these rays without agreeing as to the sign of this electrification, which is positive according to Righi, but negative according to Borgmann and Gerchun.

In view of these discrepancies, we thought it well to repeat our former experiments, greatly prolonging the action of the Crookes tube upon the gold leaves of the electroscope. We constantly observed a complete collapse, whatever was the sign of the original charge, and the complete absence of any new ultimate divergence.

Fearing a default of sensitiveness for weak charges in the electroscope, we employed a new type of symmetrical mirror electrometer* always completely enclosed in a metal cage communicating with the earth. In the interior of this cage is found, behind a window closed with a leaf of aluminium, the proof-plate which, at the outset of each experiment, is charged to a potential of about 60 volts. The dielectric which insulates the electrified bodies is absolutely protected from any action on the part of the Crookes tube.

Under these conditions, the discharge was again absolutely complete and definite, whatever was the sign of the initial charge, and whatever the nature of the metal forming the proof-plate. For we asked ourselves whether the discrepancies above mentioned might not arise from the nature of the metal. Then, if the X rays can develop an electric charge, of which we have not yet been able to observe any trace, this effect does not exceed the order of magnitude of the electrometer forces of contact.

But in the course of these new experiments, we have discovered a new specific property of different bodies, and particularly of metals in reference to the X rays. The metals being taken in discs of the same diameter, and the influence of the variations of the Crookes tube having been ascertained by the method of alternate means, we

* See "Les Rayons X et la Photographie à travers les corps opaques," Ch. Ed. Guillaume, p. 89, Fig. 16.

have observed that the time of fall from a given potential to another varies with the nature of the metal exposed. This is also the character presented by the loss of electricity under the action of the ultra-violet rays.

But the order of the different metals is not the same in both cases. It is known that, according to Leonard and Wolf, who explain these phenomena by a pulverisation of the metal, silver is the most sensitive to discharge by the ultra-violet rays; then follow gold, iron, lead, tin, copper, platinum, mercury, and zinc. But silver and zinc, which occupy the two extremities of this list, are, on the contrary, very near each other in the list which we have obtained as regards the action of the X rays, and they occupy the middle, along with gold, iron, nickel, zinc, brass, and copper. At the extremities we find, on the one hand, aluminium, in which loss is very slow; and on the other platinum and mercury, in which it is very rapid.

Here follow some figures showing the duration of one and the same fall of potential, taking as unity that of platinum:—

Zinc and brass amalgamated		0.96
Platinum, in thin plates		1.0
" in beaten leaves		1.1
Ferro-nickel		1.38
Zinc		1.41
Silver, in beaten leaves		1.41
Red copper		1.48
Silver, in plates		1.53
Aluminium, hammered		1.92
" in plates		2.12
Lamp-black		1.97

These figures are evidently in relation with the tube which we have employed, in view of the heterogeneity of the X rays which we have already demonstrated.

Hence the aptitude of the different metals to utilise the energy of the X rays for dissipating electricity distinctly varies inversely as their transparency for these rays, since aluminium is decidedly the most transparent of the above metals, whilst platinum and mercury are the most opaque. This aptitude represents a sort of absorbing power, comparable to that of bodies more or less opaque to the luminous and thermic radiations.

Further, this absorbent power has its seat in the superficial layer of the metal itself, as it increases distinctly with the thickness of this metal when such thickness is still very trifling.

Lamp-black, transparent to the X rays, is precisely as little absorbent for aluminium. Thus, the time of discharge for a plate of polished copper varies from 1.52 to 1.97 when it is coated with lamp-black.

Without, as yet, giving a complete explanation of these phenomena, in view of which we have prepared various experiments, we believe that we may present the following observations:—

1. The theory of pulverisation does not give this explanation, since it does not appear compatible with the fact observed by us, and also by J. J. Thomson, that the discharge of the electrified metals is effected completely, not only in the air, but also in a solid dielectric medium, like paraffin.

2. The property which dielectrics possess of becoming conductors under the action of the X rays—a property formulated by J. J. Thomson—does not suffice to explain all the circumstances of the phenomena, since the nature of the metal distinctly intervenes up to a certain depth. We have further observed that the relation of the times of discharge found for two different metal surfaces is not modified when the two surfaces are entirely covered with a layer of paraffin of the same thickness. We arranged to repeat this experiment, changing the nature of the dielectric covering.

The results which we have just stated seem to us to indicate in what direction future researches must be conducted in order to obtain preparations more sensitive to the X rays in photography than plates of silver gelatino-

bromide. The salts of platinum, being more absorbent, will doubtless be more advantageous, which we purpose to verify.—*Comptes Rendus*, cxxii., p. 779.

ON THE DIFFRACTION OF THE RÖNTGEN RAYS.

By L. CALMETTE and G. T. HUILLIER.

WE have the honour of submitting to the Academy some photographic proofs obtained with the Röntgen rays by means of the following arrangement:—

Very near the Crookes tube there is a screen E of brass perforated by a slit, the width of which has rarely reached a half m.m. A second metal screen, E', is formed of a plate provided with two slits or pierced with a window in which is fixed a metal rod of 1 m.m. in diameter. This screen is placed at the distance *a* behind the former. Lastly, a photographic plate, enfolded in two leaves of black paper, is placed at the distance *b* behind the second screen E'.

The following table indicates, for each proof, what is the screen E' used, and the value of *a* and *b*+*a*:—

No.	E'.	<i>a</i> . C.m.	<i>b</i> + <i>a</i> . C.m.
1. Rod of 1 m.m. in diameter..		5	19.5
3. " " " " " " " "		5	20
5. " " " " " " " "		8.9	30
7. Two narrow slits, separated by a cylindrical rod of 1 m.m. in diameter		?	?

On the proofs 1, 3, 5 the shadow thrown by the metallic rod is bordered on each side by a light band which shows a maximum of intensity. Within this shade we observe a zone less dark, which seems to indicate that the Röntgen rays penetrate into the geometrical shadow. Lastly, in proofs 3 and 5 we see, in like manner, a maximum of intensity along the margins of the window in which the rod is placed.

In the proof No. 7 we perceive, in the middle of the two white bands, a fine dark ray, whilst in the shadow of the rod which separates the two slits there is seen a light ray.

If we compare these results with those obtained with light in the same conditions, the slit being relatively wide and the intensity weak, it seems difficult not to ascribe them to the diffraction of the Röntgen rays.

The proofs obtained in these experiments—which we propose to continue—are not yet so distinct that we can measure the wave-length with any precision. But we are still led to believe that this wave-length is greater than that of the luminous rays.—*Comptes Rendus*, cxxii., p. 877.

VOLUMETRIC DETERMINATION OF THE PHOSPHORIC ACID SOLUBLE IN WATER EXISTING IN SUPERPHOSPHATES.

By C. GLASER.

THE author's process is founded on the methods of Emmerling, Kalmann, and of Meissels. The chief condition for obtaining accurate results is the addition of an excess of perfectly neutral calcium chloride, after it has been adjusted to neutrality with methyl-orange. The presence of iron and aluminium salts in large quantities has a disturbing effect, as also certain organic substances which may render the result too high. For a determination the author proceeds as follows:—

Two grms. superphosphate are repeatedly stirred up with much water, and after repeated decantation washed on the filter until 250 c.c. of filtrate are obtained: 50 c.c.

of the filtrate, after the addition of 2 drops of methyl-orange solution, are titrated with decinormal soda until the acid reaction has completely disappeared. This point is not quite easy to reach. We then add neutral solution of calcium chloride, whereon, in presence of iron and aluminium, there occurs a slight return to an acid reaction, which does not need to be regarded. We next add 5 drops of solution of phenolphthalein, and titrate with decinormal alkali until an alkaline reaction is just perceptible throughout the entire liquid. This is the correct terminal point. The alkaline reaction soon disappears again, and several more c.c. of alkali may be added until it becomes permanent; but the quantity is thus exceeded. It is advisable, in order to obtain quite sharp results, to put the liquid in quick rotation in a tall beaker, and to keep up this movement until the alkaline reaction makes its first appearance. We then read off quickly, and satisfy ourselves, by the addition of a few more c.c. of alkali, that we are not mistaken as to the final point.

On dull days it is recommended to view the liquid by concentrated light (a full, large washing-bottle).

Each c.c. of soda-lye corresponds in the first part of the titration (methyl-orange) to 7.1 m-grms. tartaric acid, and in the second (phenolphthalein) to 3.55 m-grms. If larger quantities are used, as proposed by Kalmann and Meissels, the use of semi-normal soda may be preferable. The changes of colour are then strong and more distinct. In twenty samples of superphosphate the mean result, by the above method, was 21.345 per cent soluble phosphoric acid, as against 21.256 found gravimetrically.

The attempt was made to determine the total phosphoric acid volumetrically, after previous adjustment with methyl-orange. The mean obtained was 16.65 (gravimetrically 15.50), but in some cases the discrepancies were too great, and the final reaction could not always be recognised with the distinctness desirable.—*Chemiker Zeitung and Zeit. Anal. Chemie*, xxxiv., p. 768).

ON COLOUR PHOTOGRAPHY BY THE INTERFERENTIAL METHOD.*

By G. LIPPMANN,
Professor of Physics, Faculty of Sciences, Paris.

COLOUR photographs of the spectrum, or of any other object, are obtained by the following method:—A transparent photographic film of any kind has to be placed in contact with a metallic mirror during exposure. It is then developed and fixed by the usual means employed in photography, the result being a fixed colour photograph visible by reflected light.

The mirror is easily formed by means of mercury. The glass plate carrying the film being inclosed in a camera slide, a quantum of mercury is allowed to flow in from a small reservoir and fill the back part of the slide, which is made mercury-tight. The plate is turned with its glass side towards the objective, the sensitised film touching the layer of mercury. After exposition, the mercury is allowed to flow back into its reservoir, and the plate taken out for development.

The only two conditions necessary for obtaining colour, transparency of the film, and the presence of a mirror during development, are physical conditions. The chemical nature of the photographic layer has only secondary importance; any substance capable of giving, by means of an appropriate development, a fixed colourless photograph is found to give, when backed by the mirror, a fixed colour photograph.

We may take, for instance, as a sensitive film, a layer of albumeno-iodide of silver, with an acid developer; or a layer of gelatino-bromide of silver, with pyrogallol acid, or with amidol, as developers. Cyanide or bromide of

potassium may be as usual employed for fixing the image. In a word, the technics of ordinary photography remain unchanged. Even the secondary processes of intensification and of isochromatisation are employed with full success for colour photography.

The photographic films commonly in use are found to be opaque, and formed, in fact, by grains of light-sensitive matter mechanically imprisoned by a substratum of gelatin, albumen, and collodion. What is here wanted is a fully transparent film, the light-sensitive matter pervading the whole of the neutral substratum. How can such a transparent film be realised? This question remained insoluble to me for many years, so that I was debarred trying the above method when I first thought of it. The difficulty, however, is simply solved by the following remark. It is well known that the precipitation of a metallic compound, such as bromide of silver, does not take place in the presence of an organic colloid, such as albumen, gelatin, or collodion. In reality, the metallic compound is formed, but remains invisible; it is retained in a transparent modification by the organic substances. We have only, therefore, to prepare the films in the usual way, but with a stronger proportion of the organic substratum; the result is a transparent film. By mixing, for instance, a gelatinous solution of nitrate of silver with a gelatinous solution of bromide of potassium, no precipitate is formed, and the result is a transparent film of dry gelatin containing 15 and even 30 per cent of the weight of bromide of silver.

The colours reflected by the film are due to interference: they are of the same kind as those reflected by soap bubbles or by Newton's rings. When a ray of definite wave-length falls on the sensitive plate, it is during exposition reflected back by the mirror, and then gives rise to a set of standing waves in the interior of the film, the distance between two successive loops being equal to half the wave-length of the luminous ray. This system of standing waves impresses its periodical structure on the film. The photographic deposit, therefore, takes the form of a grating, a continuous grating, perfectly adapted for reflecting the particular luminous ray which has given it birth.

This theory can be subjected to experimental proof. If we examine a photograph of the spectrum, or any other object by white light, we observe the following facts:—1. Colours are seen in the direction of specular reflection, and are invisible in every other direction. 2. The colours change with the incidence; the red changing successively to green, blue, and violet, when the incidence grows more oblique. The whole image of the spectrum is displaced, and gradually passes into the infra-red region. 3. If the film be gradually imbibed with moisture, the colour changes in the opposite direction, from red to violet. This phenomenon is due to the swelling up of the gelatin albumen, causing the intervals between the elements of the grating to become larger. The smaller intervals, corresponding to violet and blue light, gradually swell up to the values proper to red and infra-red waves. A photograph immersed in water loses all its colours, these appearing again during the process of drying. For the same reason, a freshly-prepared plate has to be dried before the correct colours can be finally seen.

We have now to consider the case of compound colours, and to generalise the former theory, which is only applicable to the action of simple rays. I beg to subjoin an abstract of this generalised theory. It will be seen that if a compound ray of definite composition impresses the plate, it gives rise during exposure to a definite set of standing waves, which impress their structure on the film, and impart to the photographic deposit a corresponding definite form. Though very complex, this can be described as made up of a number of elementary gratings, each corresponding to one of the simple rays which contribute the impressing light. When examined by white light, the reflected ray is shown to have the same composition as the impressing ray; white light, for instance, imparts

* A Paper read before the Royal Society, April 23, 1896.

to the photographic deposit such a structure that it is adapted to reflect white light.

The only *à priori* condition for the correct rendering of compound rays, is a correct isochromatisation of the film. This, again, can be practically effected by known processes, such has have been indicated by E. Becquerel, Vogel, Captain Abney, and others.

As a verification of this theory, I beg leave to project on the screen a series of colour photographs, representing natural objects: pictures on stained glass, landscapes from nature, flowers, and a portrait from life. Every colour in nature, including white, and the delicate hue of the human complexion, is thus shown to be reflected by a correctly developed photographic film.

It is to be remarked that, as in the case of the spectrum, the colours are visible only in the direction of specular reflection. If I had tried to touch up these photographs by means of water colours or other pigments, these would be made apparent by slightly turning the photograph; these pigments remaining visible under every incidence, they would thus be seen to stand out on a colourless background. Thus the touching up or falsifying by hand of a colour photograph is happily made impossible.

BERTHELOT'S CONTRIBUTIONS TO THE HISTORY OF CHEMISTRY.*

By H. CARRINGTON BOLTON, Ph.D.

MARCELLIN BERTHELOT, Professor of Chemistry in the Collège de France, Perpetual Secretary of the Academy of Sciences, Senator, Minister of Public Instruction, and recently appointed Minister of Foreign Affairs, known to the scientific world by his masterly researches in synthetic chemistry, has added to these honours that of editing the most important and far-reaching documents pertaining to the history of chemistry ever brought to light.

The six handsome quarto volumes published by him between the years 1887 and 1893 contain the most ancient Greek, Arabic, Syriac, and Latin treatises on alchemy and technical chemistry preserved in the great libraries of the Old World. Besides reproducing the original text of these precious manuscripts, these volumes contain complete translations of many treatises, analyses of the contents of others, and critical studies of their mutual relations, their sources and authorship, as well as erudite essays on the chemical knowledge exhibited in them. The six volumes form two distinct works: three of the volumes bear the title "Collection des anciens Alchimistes Grecs," and three of them "La Chimie au moyen âge," each volume having, moreover, specific sub-titles more exactly indicating its contents.

Not having seen any adequate review of these works in English, I propose in this article to examine their scope, contents, and manner of treatment, as well as to show some of the more important changes resulting from Berthelot's historical studies. The existence of ancient Greek and Arabian manuscripts had long been known; Reuvens, and later Leemans, of Holland, had published summaries of certain papyri preserved in Leyden, more than forty years before, but in such a fragmentary manner as merely to excite curiosity. Ferdinand Hoefer, the French historian of chemistry, and Herman Kopp, the erudite German, had made partial use of some of the manuscripts; but it remained for Berthelot to collect and compare the diverse copies, to reproduce and translate them for the benefit of students. This he could scarcely have accomplished without the aid of the French Government, both series being "published under the auspices of the Minister of Public Instruction." Government co-

operation was brought about through a report made by Berthelot to the "Comité des Travaux Historiques et Scientifiques," and adopted by them in 1884. This report directed attention to the existence of Greek alchemical manuscripts and to the utility of their publication, owing to the great light they throw on the history of natural science, the technology of metals and ceramics, and the history of philosophy in the first centuries of the Christian era.

The difficulties of deciphering, transcribing, and editing Greek, Arabic, Syriac, and Latin manuscripts were prodigious, and Berthelot was fortunate in securing scholars of eminence to assist in the task. In dealing with the Greek papyri, he was aided by Ch. Em. Ruelle, of the Bibliothèque Sainte Geneviève, Paris, and by André Berthelot, son of the editor; the Arabic scholar, Professor Houdas, and the Syriac linguist, Rubens Duval, also contributed their learning, each in his own sphere.

The "Collection des Alchimistes Grecs" opens with an "Introduction" by Berthelot, which occupies 268 pages; this forms an important contribution to the history of chemistry, based upon a critical study of the ancient treatises; he agrees with other historians in tracing the birth of alchemical ideas to Egyptians, whence they reached Europe through Greeks.

Certain Greco-Egyptian papyri, preserved in Leyden, are of the greatest interest; several of them treat of magical formulas, incantations, love philtres, dreams, and similar gnostic notions; one of them, known as "Papyrus X," is a treasury of information on metallurgical operations, at so early a period as the third century of the Christian era. It was found in a tomb at Thebes, secured by the Swedish Consul at Alexandria, Anastasi, and presented by him to the Netherlands in 1828. Berthelot conjectures it is one of the ancient Egyptian books on the preparation of gold and silver, which escaped the destruction ordered by Diocletian in 290,—an order issued lest the people using them should grow rich by their art and revolt against the Romans.

This precious document contains one hundred and one chemical and alchemical recipes, followed by ten paragraphs taken from Dioscorides. The recipes are for making alloys to be used in the manufacture of cups, vases, images, and other objects of the goldsmith's art, also processes for soldering metals and superficially colouring them, besides formulas for making gold and silver inks. The text is full of grammatical errors and ignorant spellings, which show the writing to have been the work of an uneducated artisan; the recipes are not arranged in order, several appear in duplicate,—they exhibit no indication of chicanery, although some of the methods are unprofitable. The whole papyrus, in short, is evidently the memorandum-book of a goldsmith (or silversmith) engaged in attempts to imitate gold and silver for fraudulent purposes. Only one author is cited, "Phimenes," who is probably Pammenes, author of recipes occurring also in other manuscripts. The preparation of *asen*, an amalgam of copper and tin, plays a prominent part among the recipes for imitating gold. But time forbids a full analysis of this remarkable manuscript; as a result of Berthelot's careful study of this and analogous treatises, he comes to the conclusion that the doctrines of alchemy concerning the transmutation of metals did not originate in the philosophical views of the constitution of matter, as generally supposed, but in the practical experiments of goldsmiths occupied in making fraudulent substitutes for the precious metals. The "Introduction" contains a chapter on the relations between the metals and the planets, of Chaldean origin, and constant occurrence in the early writings, which is illustrated by facsimiles of several manuscript pages. Another chapter is devoted to the figures of apparatus occurring in the treatises of the eleventh to fourteenth centuries; these include water-baths, digestors, aludels, alembics, and a great variety of apparatus for distillation.

* Read before the Washington Section of the American Chemical Society, March 12, 1896. Advance Proofs from *Journal of the American Chemical Society*.

The sixth chapter of the Introduction is divided into twelve sections; these deal with several Greek manuscripts, notably those preserved in the libraries of St. Mark, Venice, the Escorial, the Vatican, Rome, Gotha, and in Munich, appertaining to the eleventh to fourteenth centuries; of these we note only a few features. At the beginning of the MS. of St. Mark, in one of the earliest of chemical bibliographies, it gives the title of fifty-two treatises, verily not in modern style, yet quite suggestive; among them are the following:—"Emperor Heraclius, eleven chapters on the manufacture of gold." "Justinian, five chapters on the secret art." "Heliodorus, on the divine art." "Theophrastus, verses on this art." "Moses, on the diplosis (doubling) of gold." "Lexicon of the gold-maker, in alphabetical order."

This association of names of Emperors of Rome, Greek classical writers, and the Hebrew lawgiver, with chemical and alchemical treatises, is characteristic of the period at which they were compiled, and by no means denotes actual authorship; the names of prominent men were given to the treatises in order to add to the dignity and authority of the writings. This custom prevailed as late as the sixteenth century, and, in certain cases to be noted hereafter, gave rise to undeserved honours. An entire group of writings have been ascribed to Democritus, giving rise in Egypt to what may be styled the school of Democritus. A certain Zosimus, of Panopolis, is credited with a veritable encyclopædia of the sacred art, a work which occupies ninety pages of Berthelot's volume.

The *Collection des Alchimistes Grecs* comprises no less than 160 different treatises on the science of Hermes. Many of these are fragmentary in the extreme, extending to only six lines, and even less. All are composed in an archaic, enigmatical style, combining, in one undecipherable medley, chemical terms of obscure meaning, magical formulas, astrological notions, citations from mythical authors, and mystical allusions to a philosophy long since buried too deep for present resurrection. It is not surprising that commentators early felt the need of lexicons of the sacred art, and such are preserved in these volumes; unfortunately, however, the definitions are no clearer than the words defined; one word was often used for a score of different objects and processes, and a single article was known by a dozen different names. To convey to readers any idea of these extraordinary literary productions by citations is hardly practicable in the space available, for passages lose much when removed from their original settings. The actual chemical knowledge exhibited in these ancient manuscripts is varied, and yet indefinite owing to the numerous obscure expressions; the authors were acquainted with a large number of ores, minerals, earthy substances, and saline bodies, as well as vegetable and animal products, but their ignorance of the mineral acids and their important derivatives limited them to products obtained by aqueous solution, distillation, and the action of heat. Of scientifically classified knowledge there is no trace; the alleged opinions of mythical writers are given as authoritative, and information is imparted in the tedious form of dialogues between philosophers, who remind one of the Scotchman's definition of metaphysicians—"Poor bodies discussing things of which they know nothing in a language neither of them can understand." Many of the writings contain reverent acknowledgments of the Deity and other evidences of piety. There is a good deal of duplication, arising from the introduction into an essay of passages from another, generally without acknowledgment.

Berthelot remarks incidentally that the term *Philosophers' Stone* does not occur in writings earlier than the thirteenth century, although the central idea is much more ancient.

Each of the three quarto volumes which constitute Berthelot's "*La Chimie au moyen âge*" bears an independent title; that of the first volume reads—"Essay on the transmission of the knowledge of Antiquity to the Middle Ages; transmission of Technology; translations

of Arabico-Latin treatises, with a new version of the *Liber Ignium* of Marcus Græcus, and an original edition of the *Liber Sacerdotum*."

This volume covers the period from the fall of the Roman Empire to the thirteenth century, thus filling the gap between the ancient Greek alchemists and the Latin writers of the later epoch, a period which had been previously unworked or misunderstood. Berthelot finds that the transmission from the earlier to the later era was accomplished by two agencies; first through the Arabians, who succeeded to the literary and scientific wealth of the Greeks. The Arabic treatises, preserved in the Mohammedan libraries of Spain, were translated into Latin, and thus became for Western nations the sources of their knowledge in medicine, alchemy, mathematics, and philosophy. Some of these translations were collected and printed in the seventeenth century in the works entitled *Theatrum Chemicum* (5 vols., 1613-22), and *Bibliotheca Chémica*, of Mangetus (2 vols., folio, 1702), and Berthelot discovered in these Arabico-Latin treatises entire passages from the ancient Greek Alchemists.

The connection between the Greeks and Arabians was not, however, immediate, but through the Syrians, who were among the first to translate the philosophy and science of the Greeks into an oriental tongue. These Syriac versions form the subject of the second volume.

A second link between the Greeks and the Latin alchemy was more directly forged, though difficult of recognition; the processes used in industrial arts and metallurgical operations by the Greeks had been adopted by the Latins as early as the time of the Roman Empire, and this chemical technology was preserved through centuries of intellectual degradation to the beginning of the Middle Ages.

The most ancient Latin treatises on chemical technology are the *Compositiones ad tingenda*, dating from the close of the eighth century, and the *Mappa clavicula*, written before the tenth century. These are collections of recipes for industrial processes analogous to those in the Leyden papyrus, and forming links in a chain that extends from that ancient work through the treatises of the Middle Ages to the modern "Workshop Recipes" and "Manuels Roret's." The full title of the *Compositiones ad tingenda* is as follows: [Translation].—"Recipes for colouring mosaics, skins, and other objects, for gilding iron, for using minerals, for writing in letters of gold, for soldering metals, and other technical documents." The following are some of the subjects treated:—The colouring of artificial stones, used in the manufacture of mosaics; the manufacture of stained glass; the dyeing of skins in purple, green, yellow, and reds; the dyeing of wood, bone, and horn; a list of ores, metals, earths, and metallic oxides, used in jewellery and in painting; a number of recipes for gilding on glass, wood, skins, garments, and the metals. All these topics are treated in barbarous Latin, bordering on a species of jargon; some were originally written in Greek, and copied by ignorant scribes in Latin letters, which shows the influence of Constantinople. In one of the sections on ores the word "vitriol" occurs for the first time, being the eighth century, and in the correct significance of an impure ferrous sulphate. A very rational grouping of substances occurs in this work; the minerals and earths are by themselves; then follow gums, resins, and other products of plants; and thirdly, substances derived from the ocean, such as salt, coral, and mollusks yielding purple dye. A certain recipe for writing in letters of gold is practically identical with one in the Papyrus of Leyden.

A formula for making bronze shows the origin of this name, *De compositio brandisii*, Brindes being a synonym of Brundisium (Brindisi), a town noted in Pliny's days for its metallic mirrors.

A large part of *Compositiones ad tingenda* is reproduced in the work entitled *Mappa clavicula*, of which the earliest known manuscript dates from the tenth century. This

latter treatise contains recipes for making gold, for multiplying gold, and imitating the precious metal, closely resembling those of the ancient Greek papyri. In this connection cautions are given to conceal the secrets, and an incantation is prescribed to be used during the operation. Exceeding interest attaches to the fact that the use of the hydrostatic balance in analysis of an alloy is clearly described, for this proves that the knowledge of this instrument did not pass through Arabian channels, and possibly came down direct from Archimedes.

The *Liber ignium ad comburendos hostes*, by Marcus Graecus, is one of the most ancient Latin treatises on Greek fire, dating from the twelfth or thirteenth century, and is probably a translation from an earlier Greek work transmitted through Arabian channels. It deals with instructions for making Greek fire, so-called, phosphorescent materials, fire-proofing substances, and the preparation of fuses and petards, composed in part of saltpetre. Greek fire itself, however, dates from the second century, B.C., and phosphorescent stones are named in the much earlier Greek alchemical manuscripts.

Berthelot devotes an interesting chapter to the discovery of alcohol. This product of distillation first appears under the name *aqua ardens*, and the term alcohol in its present signification does not occur before the middle of the fourteenth century; the term *spiritus vini* is also comparatively modern, and *aqua vitae* seems to have been applied to alcohol for the first time by Arnald de Villanova, who died in 1314. The fact that wine yielded an inflammable substance was, however, already noted by Aristotle, but this body was not isolated. Rhases has been given credit for acquaintance with alcohol, but this is erroneous.

The preparation of alcohol by distilling wine is, however, mentioned in a copy of the *Mappa clavicula*, written in the twelfth century, and in the *Liber ignium* of Marcus Graecus.

In attempting to trace to their origin Latin treatises which claim to be translated from Arabic, Berthelot made the important discovery that they are fraudulent, the Arabic manuscripts having no existence. Thus the chemical works attributed to the Arabian physician Jabir ibn Hayyan (Abu Musâ), commonly called Geber, are shown to be fictitious, and the great reverence paid to him as a pioneer in chemistry has been misplaced. The whole history of chemistry has been falsified by giving credit to the Arabians for knowledge which really belonged to a period five hundred years later.

Yet the historical personage Geber, who lived in the ninth century, left many treatises in Arabic, now preserved in Paris and Leyden, and the translation of these occupy 100 pages of the third volume; they are very different from the works so widely known as Geber's, which are found in Latin, French, German, and English.

In like manner the current alchemical treatises ascribed to Raymond Lully are shown to be fictitious, yet his works on philosophy in the Provençal language are extant.

The pseudo-Arabic works in their Latin form contain, however, traces of the ancient Greek alchemical writings, and to endow them with authority the writers referred the text to mythical personages; and as these were cited by later authors who did not doubt their genuineness, the pseudo-treatises acquired undeserved renown. Students of alchemy who have been revelling in the works of Morien, Kalid, Zadith, Mary, and the collection of citations entitled *Turba philosophorum*, are loth to have their antique idols shattered, but this is the fate of every branch of human knowledge when subjected to the modern methods of searching analysis.

The second volume of "La Chimie au moyen âge" has the sub-title, "Syriac Alchemy, comprising an introduction, and several treatises of Syriac and Arabic alchemy from the manuscripts in the British Museum and Cambridge; text and translation."

The existence of Syriac alchemical manuscripts in the British Museum was pointed out to Berthelot by Prof.

Richard Gottheil, of Columbia University, New York City. The most important of these, entitled "The Doctrine of Democritus," was translated from Greek between the seventh and ninth centuries. It begins with a charge of self-purification, followed by a key to the symbols used in the manuscript; these signs resemble in part those occurring in the writings of the earlier Greek alchemists. The first section of the "Doctrine" is called "The Preparation of Gold," the second is called "On the Philosophers' Stone," and the succeeding parts contain a collection of recipes, processes with metals, as well as with sulphur, antimony, arsenic, and ores, analogous to the Leyden papyrus and the *Mappa clavicula*. Rude drawings of apparatus accompany the text. The writer shows acquaintance with a very large number of chemical substances.

The Library of the University of Cambridge possesses a Syriac manuscript, which is a translation of portions of the Greek writings of Zosimus, Democritus, and others. It is similar in character to the preceding.

Volume III. of "La Chimie au moyen âge" has the sub-title, "Arabian Alchemy, comprising an historical introduction, the treatises of Crates, el-Habib, Ostanès, and Djâber, from manuscripts in Paris and Leyden; text and translation."

The Arabic treatises here named are the genuine writings, not the fictitious ones known only in Latin. The first Mohammedan writer on alchemy was Khâled ben Yezid ibn Moaouïa, Prince Omeyyade, who died in 708; he is a historic personage and the reputed teacher of Djâber. Only the titles of his works have come down to us. Djâber, the Geber of the Latins, was, however, the great master of the art and enjoyed the highest reputation throughout the Middle Ages; he is credited with 500 treatises, an Oriental exaggeration. Six of these are here collected and translated. They exhibit evidence of Moslem faith on the part of the author; he shows familiarity with the hydrostatic balance, with many species of minerals (of which an ingenious classification is given), and he discourses on the changes in volume produced by heat and by cold; at the same time he admits using allegorical and obscure language in all his works. There is no reference to the mineral acids, to nitrate of silver, and other chemicals that Geber is supposed to have known. Perhaps the most clever passage in his works is the following from the "Book of Mercy":—

"I saw that persons engaged in attempts to manufacture gold and silver were working ignorantly and by wrong methods; I then perceived that they were divided into two categories, the dupers and the duped. I had pity for both of them."

Berthelot's superb volumes comprise more than 2600 pages, and much of the contents defies review. Besides these original documents, he has published two works dealing in more popular style with the periods of alchemy and Middle Age chemistry. These are entitled: "Les Origines de l'alchimie" (1885), and "Introduction à l'étude de la chimie des anciens et du moyen âge" (1889); the latter is largely reprinted in the quarto volumes; all are charmingly written, well illustrated, and well indexed.

Berthelot had extraordinary qualifications for the task and enjoyed unrivalled opportunities; the result is a magnificent contribution to the history of chemistry, of utmost interest to the chemical student as well as to the philosopher.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 206).

Carbonate of Thallium prepared by Mr. Crookes.—I proceeded to purify this carbonate by the method of suc-

cessive crystallisations. This salt contained sensible quantities of barium, calcium, and sodium, probably in the form of silicates. After six crystallisations, I succeeded in volatilising the carbonate of thallium without finding a trace of the barium or calcium spectra, moistening with chloride of ammonium the platinum spiral used to carry the salt, and introducing it into a hydrogen flame after the thallium had been volatilised. The carbonate, when freed from barium and calcium, showed the sodium line very strongly and persistently. Five re-solutions in pure water, followed by precipitation by absolute alcohol, were not sufficient to prevent the appearance of the sodium line; moreover, on volatilisation it left a small, very fusible, solid residue, which coloured a hydrogen flame yellow, and showed, on spectrum analysis, the sodium line only. I was obliged, from want of material, to abandon my efforts to obtain, from the carbonate sent me by Mr. Crookes, this thallium salt in such a state of purity that it would not show the sodium line. I took up this subject again, using carbonate prepared by myself.

Mr. Crookes's Metallic Thallium.—I checked the preceding results by means of some of the metal prepared by Mr. Crookes. I submitted Mr. Crookes's metal, and some commercial metal I obtained, to the same treatment, as follows:—The thallium to be purified was dissolved in dilute nitric acid, and the solution evaporated to dryness in a porcelain dish. The residue was converted into sulphate by means of a proper quantity of pure sulphuric acid. The resulting salt, consisting of a mixture of thallous and thallic sulphates, was heated to dryness in a platinum vessel. I dissolved the residue in boiling water, and passed a current of sulphurous acid into the solution, which was kept at a high temperature, until it emitted a strong smell. Under the influence of the sulphurous acid, the liquid, which was clear, became very much clouded, forming a white precipitate consisting entirely of sulphate of lead.

After completely cooling, the solution, diluted with water to re-dissolve the sulphate that had crystallised, was filtered, and the clear liquid was heated, and kept at boiling-point until the sulphurous acid was completely eliminated. This result being obtained, I added sulphuric acid; this coloured it a deep brown. When put into a closed flask and left alone, it lost its colour, depositing a black sulphide, consisting of a mixture of sulphides of lead, mercury, silver, thallium, cadmium, and zinc. I saturated the clear liquid in the cold with sulphuric acid; it no longer became coloured, even after twenty-four hours' exposure to light in a closed vessel, and it deposited nothing. The sulphuric acid was driven off by the action of heat, and the sulphate, when re-cooled, was poured into a slight excess of hydrochloric acid to precipitate the thallium.

The chloride produced was washed, first by decantation with water containing 6 per cent of its volume of hydrochloric acid, and then with a wash-bottle, using the same liquid.

The mother-liquor and the washings were evaporated, and the residue examined; it contained a notable amount of zinc, with traces of cadmium and iron.

Thallous chloride when washed as well as possible, still retains sulphuric acid; therefore it may also contain sulphate of zinc, &c. I therefore converted it into sulphate by heating it in a porcelain dish with a suitable quantity of pure sulphuric acid. The salt thus obtained was in the form of monothallous sulphate; I heated it in a platinum dish so as to reduce it to bithallous sulphate. I found that this conversion required great care, because very considerable quantities of thallium might be carried off with the sulphuric acid fumes, and make the air unbreathable.

The thallous sulphate was taken up in boiling water, and the solution again poured into an excess of hydrochloric acid. The chloride deposited on quickly cooling was washed as before, and again transformed into thallous sulphate, and this in its turn into thallous chloride. I

repeated this transformation a third time, because I found a sensible quantity of zinc in the residue left after evaporating the mother-liquor of the second precipitation and the washings from the thallous chloride.

I re-converted the chloride from the third precipitation into thallous sulphate. The transformation of monothallous into bithallous sulphate having had to be effected in platinum, and this metal being slightly attacked by monothallous sulphate, the salt obtained contained a sensible quantity of platonic sulphate.

To eliminate this last metal, I had recourse to the successive actions of sulphurous and sulphuric acids. With this object I kept the solution of thallous sulphate, with the addition of sulphurous acid, at about 100° for several hours. After having thus reduced the platonic sulphate into platinoso-platonic sulphate, which could be precipitated at once by sulphuric acid, I drove off the excess sulphurous acid by heating it, then adding sulphuric acid.

The solution was coloured brown; it was kept on a bath at 100° in a closed flask, until the liquid became colourless owing to the separation of the platinoso-platonic sulphide: this took place slowly, but completely, carrying off a sensible amount of thallous sulphide.

After it became colourless, I filtered the sulphate solution, and heated it to drive off the dissolved sulphuric acid.

It appears, then, that the separation of foreign metals from thallium is a laborious and very delicate operation.

The examination to which I subjected the solution of thallous sulphate enabled me to detect the presence of alumina and soda, due undoubtedly to the attack on the porcelain dishes used during the transformation of the chloride into thallous sulphate. I eliminated the alumina by means of pure ammonia, and then had recourse to successive crystallisations of the sulphate in order to get rid of the sodium. It needed five crystallisations, removing the mother-liquors each time and washing it, before the sodium line was no longer visible in the spectrum of the salt obtained.

I used the sulphate produced thus to obtain:—

- 1st. Metallic thallium. For this purpose I had recourse to electrolysis of the ammoniated solution, as I mentioned before.
- 2nd. Brown or black thallic hydrate.
- 3rd. Thallous chloride, precipitated and then re-dissolved three times in boiling water; immediately after its preparation it showed no trace of the sodium line.
- 4th. Thallous bromide. I find that there are three very distinct physical states of this bromide: the first is white; it is formed when an excess of thallous sulphate is precipitated by hydrobromic acid: the second is pure yellow, but very light; it is formed when dissolved thallous sulphate is poured in the cold into an excess of dilute hydrobromic acid: the third is a slightly yellowish white; it is formed when either white or yellow bromide is dissolved in boiling water, or when either of these bromides is exposed under water to direct sunlight.

Light has no decomposing action on thallous bromide, at least when it does not contain bromide of silver. Immediately after its formation and washing, it shows, on spectrum analysis, no trace of the sodium line; it is the same, in this respect, if it is kept under water in a closed vessel. When left in free air, it shows the sodium line on spectrum analysis after a few days.

- 5th. Iodide, by double decomposition with pure iodide of ammonium. Iodide obtained by pouring a solution of iodide of ammonium into an excess of dissolved thallous sulphate is yellowish white, unaltered by light; it contains sulphate mixed with it, and a long digestion in water at 100° cannot entirely remove it. Iodide produced by pouring a solution of thallous sulphate into an excess of iodide of ammonium is dirty yellow,

unaltered by light; it also contains thalious sulphate: this can be separated by allowing it to remain in the cold in a dilute solution of iodide of ammonium. After long-continued action of iodide of ammonium, it is a more pronounced and purer yellow. When washed then with water, and introduced into a hydrogen flame, it shows the thallium spectrum only. When left in the air under a bell-jar, it shows the sodium line after a few days.

From the metallic thallium obtained by electrolysis of sulphate that had been submitted to five successive crystallisations, removing the mother-liquor each time, I procured:—

1st. A solution of thalious hydrate. I prepared this hydrate by exposing well-washed, crystallised, and sodium-free thallium to the action of purified air and water, in a covered platinum crucible, under a bell-jar. The metal, being half covered with water, was at first very bright, but tarnished rapidly, and at last was quite black; after a few days it had completely disappeared. At the bottom of the colourless and very alkaline liquid was a small quantity of hydrate of the black trioxide. The thalious hydrate solution showed, on spectrum analysis, persistent signs of the presence of sodium in the flame, although the colour imparted to it by the hydrate was remarkably pure in tint and characteristic of the thallium flame.

It was impossible to evaporate the solution to dryness in platinum or gold without attacking those metals.

2nd. Dissolved and crystallised thalious carbonate. To prepare this salt, I left some thallium under a bell-jar, in air containing carbonic acid, half immersed in pure water in a covered platinum vessel. The metal is entirely transformed into carbonate, which dissolves completely if there is enough water. The solution is colourless, and although prepared from metal, water, and carbonic acid, which show no trace of the sodium line, yet it shows persistent signs of the presence of sodium, doubtless occluded from the air in the bell-jar.

It is sufficient to precipitate the carbonate first by absolute and then by dilute alcohol, and to wash it thoroughly with alcohol at 90°, in order to obtain a powdery salt, which can be entirely volatilised without showing the slightest trace of the sodium line.

I will repeat here what I have already mentioned—the absence of the sodium line is no proof of the absence of sodium from the carbonate.

Crystallised or powdery pure carbonate of thallium is colourless, and may be exposed to direct sunlight without becoming coloured. When left for several days in air under a bell-jar, it shows unequivocal signs of the presence of sodium.

3rd. Dissolved and crystallised thalious nitrate. I obtained a solution of this salt by treating the pure metal with nitric acid distilled directly into a recently-heated platinum vessel. The solution, immediately after its production, showed no trace of the sodium line. When left to evaporate under a bell-jar by the side of a dish of sulphuric acid, it forms colourless prisms, unaltered by air and light. These prisms, when introduced into a hydrogen flame, give absolute indications of the presence of sodium.

The aqueous solution of crystallised nitrate, when poured into pure absolute alcohol, yields, after being properly washed with alcohol at 90°, a powdery precipitate which, when introduced into a hydrogen flame, shows, on spectrum analysis, no trace of the sodium line.

The phenomena shown by all the thallium compounds mentioned above, corroborate the observations made on the presence of sodium in air, and the condensation of it

by bodies which are exposed to it for a certain time. Thus thallium compounds condense it by contact with air like every substance I have carefully examined.

(To be continued).

ON THE QUANTITATIVE ESTIMATION OF TIN.

By CECIL J. BROOKS.

THE following is a brief record of experiments made in the laboratory of Messrs. Stanger and Blount to ascertain the cause of the low results which are often obtained in the determination of tin.

Pure tin being difficult to procure, a good sample of the commercial material was used, which gave the following composition on analysis:—

Tin	99.25 per cent.
Lead	0.36 "
Copper	0.10 "
Iron	0.06 "

Fifty grms. were treated with a small quantity of hydrochloric acid, to avoid the formation of stannic compounds and the solution of impurities; this was kept as a stock solution of approximately known strength; a dilute solution was prepared from this, and was standardised by evaporating 50 c.c. with excess of sulphuric acid, oxidising with nitric acid. Evaporating again with sulphuric acid, and igniting in a gas muffle until the weight of the residue (stannic oxide) was constant, giving a total weight of 0.4508 gm., i.e., 0.00901 gm. of stannic oxide per c.c.

Experiment I.—50 c.c. of the solution were acidulated with hydrochloric acid, and a large volume of hydrosulphuric acid added; the gas was then passed for some time; finally the solution was heated, filtered, and the precipitate of stannous sulphide washed until the washings were no longer acid, dried, and ignited slowly. As the filter-paper burned, the precipitate broke up with some violence; and after ignition in the muffle gave 0.4467 gm. stannic oxide, the loss being therefore 0.0041 gm. (of stannic oxide).

Experiment II.—50 c.c. were taken, about 10 c.c. of nitric acid (sp. gr. 1.42) added, and the mixture was boiled and precipitated as in Experiment I. It was found that no oxidation had taken place; after the precipitate weighed 0.4451 gm., the loss being in this case 0.0057 gm.

As it was seen from this that oxidation with nitric acid did not take place readily, some of the solution was boiled with acid of different strengths, and it was found that oxidation depended on the dilution rather than on the quantity of acid present.

1. A solution measuring 105 c.c., and containing 0.035 gm. of tin, was boiled with 1 c.c. of nitric acid (sp. gr. 1.42), and gave no indication of oxidation when precipitated with hydrosulphuric acid, the bulk of the precipitate being stannous sulphide.

2. A solution of 55 c.c., and containing 0.035 gm. of tin, when boiled with 1 c.c. nitric acid, gave no indication of oxidation.

3. A solution of 25 c.c., and containing 0.035 gm. of tin, when boiled with 1 c.c. nitric acid, showed partial though slight oxidation.

Bromine was found to be a more effective oxidising agent. Potassium chlorate and hydrochloric acid also acted readily.

My attention was now directed to the possible volatilisation of stannic sulphide on ignition. A specimen was therefore prepared. It was noticed that the thin cakes of stannic sulphide left on drying on the filter, broke up violently when gently heated; in fact, the warmth of the hand was sufficient to cause them to decrepitate.

The sulphide was finely powdered, and heated in a porcelain tube attached to a long glass tube, so that any volatile products (other than sulphur dioxide) might be caught. Oxidation was performed by means of a slow stream of air; the temperature ranged from well below redness to about the melting point of gold. At the close of the experiment it was found that 5.5 per cent of stannic oxide had been volatilised.

It is clear that the ease with which stannic and stannous sulphides are volatilised on roasting is the cause of the difficulty often experienced in the determination of tin, and to overcome these difficulties the following process was adopted:—

Fifty c.c. were acidulated and oxidised with bromine, whilst hot hydrosulphuric acid was added, and the gas passed. The solution was filtered and the precipitate washed, dissolved off the filter with hot ammonium sulphide; the solution evaporated in a weighed basin to a convenient bulk, oxidised with nitric acid, and the residue (stannic oxide) dried, ignited, and weighed.

First determination gave 0.4495 grm. stannic oxide.

Second " " 0.4519 " "

These numbers show a fair concordance with the weight taken as a standard, 0.4508 grm. of stannic oxide. As a final test, 0.25 grm. of the same tin was taken and treated as above; and after the subtraction of impurities present in the stannic oxide (lead being calculated as sulphate and copper as oxide) the following result was obtained:—

Tin found.	Calculated.
0.2490	0.2489

The method, though lengthy, appears to be accurate.

REMARKS ON THE LIQUEFACTION OF HYDROGEN, AND ON THE USE OF VACUUM VESSELS.

By Dr. H. KAMERLINGH ONNES.

AFTER referring to the work of MM. Solvay, Cailletet, and Dewar, on liquid hydrogen, and of Van Marum, who first succeeded in liquefying one of the permanent gases, the author mentions that "The temperature to which the hydrogen can be cooled and the quantity available per unit of time being given, the most advantageous construction of the apparatus to cool the hydrogen further by its own expansion can be studied by means of a model, using a more suitable substance at a more convenient temperature, and applying my theorem concerning Van der Waals' law of corresponding states."

By applying this theorem he shows that the reversing point of the sign of the specific heat of saturated vapour is not in general found at corresponding temperatures in different groups of substances. The author then points out that the application of this theorem to the design of apparatus for liquefying hydrogen presents certain practical difficulties. "For instance, gravity is no corresponding force for two substances in corresponding states. The mutual accelerations by the effect of the molecular forces of two pairs of molecules of substances in corresponding states, when these pairs of molecules are in conform situations, will be expressed for each pair by the same number, when measured with the unit of acceleration proper to the system. But the acceleration of gravity will in general be represented by different numbers when measured in the two cases by the said units, and the similarity in the motion will be disturbed. The theorem therefore can only strictly be applied if the influence of gravity (and accordingly also the influence of convectional transport of heat) is to be neglected.

"And, lastly, it will not be possible in general to obtain walls of such conductive power and such specific heat

that these can give off corresponding quantities of heat in corresponding times.

"Still with these restrictions it can be of use, in the questions we have in view, to consider the gas in the machine as part of the machine itself."

After describing his own apparatus, which led to no good results, and comparing it with Solvay's apparatus, which was designed on similar principles and was also unsatisfactory, the author comes to Linde's method, in which the gas flows from a compressor under high pressure, along a regenerative coil and through a reducing valve, where it does work against the molecular forces, and is accordingly cooled, and then returns by the regenerative coil to the compressor. Now according to the theory published by Van der Waals in 1873, applicable to the ordinary temperature, the Linde apparatus, instead of cooling, should heat hydrogen gas streaming through the reducing valve.

After considering the effect of introducing this gas at low temperature into the apparatus, Prof. Waals has given a new value for the molecular attraction, viz.—

$$a_k e \frac{T_k - T}{T_k},$$

where a_k is a constant, T the absolute temperature, and T_k the critical temperature of the substance, so that "a" increases when the temperature decreases. This theorem predicts, for hydrogen and low temperatures, a relatively great molecular potential energy, and consequently a sensible cooling, in Joule and Thomson's experiment, and a good working of the Linde apparatus. After a pretty full description of the working of a Linde apparatus, the author enlarges on Prof. Dewar's work, which he evidently considers of great importance.

Prof. Dewar, he mentions, begins with much higher pressures than Linde, and expands his gas down to the ordinary pressure, thus wasting still more power than Linde, and departing still more from the theoretically most favourable cooling process, with even better results.

He goes on to say, "In my boiling-glass, just as in Dewar's apparatus, the supply-coil has a cock at the end, and is wound round the cock supporter. This part of my apparatus is also immersed in the gas flowing away. What is blown away from the jet as liquid must serve to cool the supply-coil, and further to take away heat that would otherwise find its way to the bath of liquid oxygen. But in the supply-coil the oxygen is already in the liquid state.

"The spiral was therefore shortened to only such length as seemed necessary to catch the liquid blown away, and to utilise the evaporation of this liquid to cool the adding coil. Dewar, on the contrary, has not been discouraged by the less economical employment of gas, and, armed with his vacuum vessel that leaves the returning gas wholly disposable to cool the coming gas, has directed his attention exclusively to the lowering of the temperature. He succeeded in this manner even in freeing oxygen by means of his hydrogen spray—a splendid outcome of his prosperous researches."

After applying the theorem of the corresponding states of Van der Waals to calculate the quantity of hydrogen that may be expected to be reduced to the liquid state in this apparatus in a certain time, the author mentions Dewar's vacuum vessels, which he states to be the most important addition since 1883 to the appliances for low temperature research.

"The vacuum jackets make it easy to work with liquid oxygen in a different room from where the cryogenic apparatus is placed, and enable one to do this even in other laboratories. . . . In many cases vacuum jackets can also be used to improve the construction of my boiling-glass, in making the evaporation of the bath less than it is without this appliance."

After suggesting some further uses to which the vacuum jackets might be applied, the author concludes by hoping that practical engineers will soon feel the want of these

non-conducting mantles; for, as he says, "As soon as this stage is reached, numbers of heads and hands are disposed to take over the problem from the scientific researcher."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Anniversary Meeting, March 26th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

THE PRESIDENT commenced his address by alluding to his early connection with the Society as one of its Secretaries in 1865, when the meetings were held in the buildings of the original Burlington House, and mentioned the fact that it was during his period of office that the change to the present rooms was made. He touched upon the original intention of the Society to found a Chemical Museum, an idea ultimately abandoned; and on the use of the preparation room attached to the meeting room.

Allusion was made to the increased interest attaching to communications illustrated experimentally, and to some of the communications made during the past year which had been so illustrated.

The difficulty arising from the large number of papers now received for reading at the meetings was mentioned, and means were suggested by which this difficulty might partly be met.

The fees for composition, which were unduly low, had now been put on a proper basis.

The communications which had passed between the Council and their French neighbours and colleagues, first on the occasion of M. Pasteur's death, and again on the celebration of the hundredth anniversary of the *Institut* were mentioned.

The decision of the Council to publish a Collective Index of the publications from 1873 to 1892 in two volumes was referred to, and the hope was expressed that both volumes would be delivered to the Fellows entitled to them during the coming year.

Reference was made to the private issue of lists of names calling attention to some of the candidates proposed for election. The feeling of the Council was strongly adverse to the issue of such anonymous appeals.

The arrangements for the publication of the *Proceedings* at the Jubilee of the Society which had been drawn up, and to a large extent completed, by Dr. Armstrong, were mentioned. The record will, it is hoped, consist of two volumes; the first of which, containing a report of the speeches made at the Jubilee meeting and at the dinner which followed, and an account of the early history and development of the Society, is all but complete. The second would consist of an account, written by Dr. Armstrong, of the scientific work of the Society during the first fifty years of its existence.

The Society has lost two of its Foreign Members, Lothar Meyer and Pasteur. A memorial lecture in connection with the former will be delivered by Professor Bedson, on May the 28th; and arrangements are in progress for the delivery of a similar address in connection with Pasteur. Reference was made to Professor Fitzgerald's address on the life and work of von Helmholtz, to the forthcoming celebrations in connection with the completion of Lord Kelvin's fiftieth year as Professor of Natural Philosophy in the University of Glasgow, and to the seventieth anniversary of the birth of Cannizzaro.

It was pointed out that the action of the new by-law under which Fellows whose last year's subscription was in arrear were removed from the register, had tended to keep down the numbers of the Society.

The numerical strength of the Society was as follows:—

Number of Fellows, March 31st, 1895	1979
since admitted	116
reinstated by Council	9
	2104

Removed on account of non-payment of three annual subscriptions	28
Do. two annual subscriptions	19
Withdrawn	23
Deaths	15
	85

Number of Fellows, March 31st, 1896	2019
Foreign Members	28

The Society was fortunate in having been deprived of only fifteen of its Fellows by death:—Cave, Herbert; Davy, S. H. M.; Galloway, R.; Kelly, J. A.; Liepmann, Hy.; Linford, J. S.; Looker, P.; McRoberts, G.; Morgan, Wm.; Offord, J. A.; Pochin, H. D.; Smith, C. H.; Smith, M. H.; Winstone, A. B.; Wood, John.

Twenty-two Life Members have not responded to requests for their present addresses, and it has been decided that if a renewed effort to reach them is unsuccessful their names will be removed from the register. Their names are:—Bell, P. C.; Bosanquet, R. H. M.; Brown, Prof. F. D.; Chester, E. D.; Cowie, T. R.; Crampton, Geo.; Custance, Prof. J. D.; Danson, J.; Edwards, J. B.; Emmons, H.; Frost, R.; Hadkinson, J.; Marsh, C. W.; Newton, H.; Strangman, J. P.; Tomlin, A.; Tookey, C.; Watson, W. H.; Williams, T.; Young, B.; Millar, James; Vacher, Arthur.

The number of communications made to the Society during the year was 163.

One hundred and sixteen papers were published in the *Transactions* for 1895, occupying 1172 pages, whereas in the preceding year 83 papers were published, occupying 1039 pages.

The following were the statistics relating to the Abstracts:—

PART I.		Pages.	No. of Abstracts.
Organic Chemistry		692	1190
PART II.			
General and Physical Chemistry			318
Inorganic Chemistry			234
Mineralogical Chemistry			97
Physiological Chemistry			174
Chemistry of Vegetable Physio- logy and Agriculture			110
Analytical Chemistry			359
Total in Part II.		544	1292
Total in Parts I. and II.		1236	2482

The Index to the *Transactions*, *Proceedings*, and *Abstracts* occupies 175 pages.

As showing the use made of the Library, it was announced that 675 volumes were borrowed from it. 134 books, 504 volumes of periodicals, and 105 pamphlets were added to the Library.

A new system of registration has been adopted, which, it is hoped, will prevent any further loss of books.

Dr. GLADSTONE, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed.

Professor DIXON, F.R.S., seconded the motion, which was carried by acclamation.

The PRESIDENT having thanked the meeting, Professor THORPE, F.R.S., the treasurer, gave an account of the balance sheet, which he laid before the Society, duly audited.

The receipts had been:—By admission fees and subscriptions, £4454; by sale of Journal and advertisements, £511 8s. 3d.; and by dividends on invested capital, £381 15s. 9d. The expenses had been:—On account of the Journal, £2858 10s. 6½d.; on account of the Proceedings, £261 6s. 2½d.; on account of the General Index, £184 2s. 6d.; on account of the Library, £306 17s. 4d.; the total expenditure being £4406 18s. 2d. Grants amounting to £180 had been made to the Fellows from the Research Fund during the year.

Mr. TYRER proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Mr. D. HOWARD, and carried.

The TREASURER, in responding, proposed a vote of thanks to the auditors.

Mr. A. BLOXAM seconded the motion, which was unanimously adopted, and acknowledged by Mr. B. BLOUNT.

Dr. RUSSELL, F.R.S., proposed a vote of thanks to the Officers and Council.

Professor TILDEN, F.R.S., seconded the motion, which was unanimously adopted.

Professor THOMSON responded.

Professor McLEOD, F.R.S., proposed a vote of thanks to the Editor, Sub-Editor, and Abstractors, which was seconded by Dr. THORNE, and carried.

Mr. GROVES, F.R.S., responded.

Dr. J. Voelcker and Mr. Nagel were appointed scrutators, and a ballot was then taken for the election of Officers and Council for the ensuing year. The following were subsequently declared duly elected:—

President—A. Vernon Harcourt, M.A., LL.D., D.C.L., F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, LL.D., Ph.D., F.R.S.; A. Crum Brown, D.Sc., M.D., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Lord Playfair, K.C.B., Ph.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—Horace T. Brown, F.R.S.; James Dewar, M.A., LL.D., F.R.S.; Francis Robert Japp, M.A., Ph.D., LL.D., F.R.S.; Ludwig Mond, F.R.S.; W. Chandler Roberts-Austen, C.B., F.R.S.; William A. Tilden, D.Sc., F.R.S.

Secretaries—John M. Thomson; Wyndham R. Dunstan, M.A., F.R.S.

Foreign Secretary—Raphael Meldola, F.R.S.

Treasurer—T. E. Thorpe, LL.D., F.R.S.

Other Members of Council—P. Philips Bedson, D.Sc.; Bennett Hooper Brough; Bernard Dyer, D.Sc.; Otto Hehner; Herbert McLeod, F.R.S.; H. Forster Morley, M.A.; G. Harris Morris, Ph.D.; James Wyllie Rodger; W. A. Shenstone; Arthur Smithells, B.Sc.; Thomas Stephenson, M.D.; Sydney Young, D.Sc., F.R.S.

CORRESPONDENCE.

COLOUR OF THE IONS AS A FUNCTION OF ATOMIC WEIGHT.

To the Editor of the Chemical News.

SIR,—Your abstract of a paper from the *Zeit. Anorg. Chemie*, by Julius Thomsen (CHEMICAL NEWS, vol. lxxiii., p. 198), gives one to understand that a proposal has been made to reject the present form of the periodic classification of the elements, and also that another form of it has been proposed based on the colour of the ions. Will you permit me to say that, after giving years of study to the relations which exist between the colour and chemical

constitution of bodies, many of my contributions to the subject having appeared in this journal, I am in the habit of dilating on Carnelley's Periodic Law of Colour as one of the grandest examples in support of the natural or periodic classification of the elements in its usual textbook form. Here colour is directly seen to be a function of atomic weight, and it is a property that does not want weighing or laboriously ascertaining for the purpose. I am dealing with this matter fully in my work on "The Old Light and the New" (Chapman and Hall, Ltd.), now in the press, and also with its bearing on X-ray phenomena.—I am, &c.,

WILLIAM ACKROYD.

NOTICES OF BOOKS.

Comparative Cost in Chile of Gas and Electricity, and Systems for the Distribution of Energy. ("Koste Komparatibo en Chile del Gas i de la Elektrizidad komo Sistemas de Distribuzion de Enerjia.") By A. E. SALAZAR and K. NEWMON. Santiago de Chile. 1896. 8vo., pp. 72.

THIS pamphlet reminds us of our old acquaintance the "Fonetic Nuz." It is written in a "reformed" version of orthography, and will hence be found somewhat perplexing even to persons by no means ignorant of the Spanish tongue. The authors conclude that in countries like Chile—where gas-coal is scarce, costly, and of mediocre quality, and where good coal has to be imported—an undertaking for the distribution of electric energy, independent and well organised, may be more profitable as a business than that of gas, or for an equality of profit realised may offer to the public a superior commodity at a less price. Coal of ordinary quality may be had at 10 per cent. less money than the coal used in the manufacture of gas.

Hydraulic power cannot be had gratuitously in Chile, and its adoption requires a previous comparative study of its advantages as compared with other means of energy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 14, April 7, 1896.

Observations on the X Rays.—Silvanus P. Thompson.

On Electrified Röntgen Rays.—A. Lafay.—Already inserted.

A Condition of the Maximum Power of Crookes's Tubes.—James Chappuis and E. Nugues.—Already inserted.

Thermic Study of some Oxybromides.—M. Tassilly.—Not adapted for useful abstraction, and not of sufficient importance for insertion in full.

Action of Hydrobromic Acid and Hydriodic Acids upon Phosphonyl Chloride.—A. Besson.—The action of HBr on POCl₃ enables us to obtain the entire series of substitution products, POCl₂Br, POClBr₂, POBr₃, and PBr₅.

On Rice Preserved for upwards of a Century.—M. Balland.—The rice in question is paddy, non-decorticated. The fatty matters tend to disappear, while the acidity was not appreciably modified.

No. 15, April 13, 1896.

On Fallows.—P. P. Dehérain.—The author shows that the practice of fallowing was well adapted to the con-

ditions of former times, but that it has lost its uses since nitrate of soda and generally mixed manures have become available.

On Nitrates in Spring Waters.—Th. Schloesing.—This memoir requires the two accompanying illustrations.

Products of Combustion of an Acetylene Burner. Explosive Mixtures of Acetylene and Air.—M. Gréhan.—If we wish to make use of acetylene we must very carefully avoid the detonating mixtures which it forms with air, and which may occasion disastrous accidents.

On Electrified Röntgen Rays.—A. Lafay.

Action of the Röntgen Rays on Double and Three-fold Electric Layers.—M. Piltchikoff.

Mechanical Action emanating from Crookes Tubes.—A. Fontana and A. Umani.—(See p. 211).

Application of Photography with the Röntgen Rays to the Analytical Research of Vegetable Matters.

Upon Hemolinalol, and on the Constitution of Licareol and Licarhodol.—Ph. Barbier and L. Bouveault.—This memoir does not admit of useful abstraction.

MEETINGS FOR THE WEEK.

- MONDAY, 11th.**—Society of Arts, 8. (Cantor Lectures). "Applied Electro-Chemistry," by James Swinburne.
— Medical, 8. (General Meeting).
- TUESDAY, 12th.**—Royal Institution, 3. "Ripples in Air and on Water," by C. V. Boys, F.R.S.
— Society of Arts, 8. "Wood Engraving as compared with other Reproductive Art, and its Future as a Fine Art," by W. Biscombe Gardner.
— Medical and Chirurgical, 8.30.
— Institute of Civil Engineers, 8.
— Photographic, 8.
- WEDNESDAY, 13th.**—Society of Arts, 8. "Tunnelling by Compressed Air," by E. W. Moir, M.Inst.C.E.
— Geological, 8.
- THURSDAY, 14th.**—Royal Institution, 3. "The Art of Working Metals in Japan," by W. Gowland, F.C.S.
— Society of Arts, 4.30. "Tea Planting in Darjeeling," by G. W. Christison.
— Institute of Electrical Engineers, 8.
— Mathematical, 8.
- FRIDAY, 15th.**—Royal Institution, 9. "Cable Laying on the Amazon River," by Alexander Siemens, M.Inst.C.E.
— Quekett Club, 8.
- SATURDAY, 16th.**—Royal Institution, 3. "Three Emotional Composers—II. Wagner," by F. Corder, Curator, Royal Academy of Music.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1903.

ON THE EXISTENCE OF THE RÖNTGEN RAYS IN ORDINARY SUNLIGHT.

By Dr. T. L. PHIPSON.

SOME readers of the CHEMICAL NEWS may, perhaps, remember that in the year 1881 (June, August, and September) I made some experiments upon a new white pigment containing sulphide of zinc and barium sulphate, and that its extraordinary behaviour with regard to sunlight made me suspect that it contained some compound of a new element, to which I gave provisionally the name of *Actinium*. I did not succeed in obtaining this new element in an isolated form, and circumstances compelled me to abandon the experiments for a time. Anyhow, these experiments proved that there exists in this white pigment some compound on which light acts in a very peculiar manner, as I made known at the time. *Sunlight darkens this compound, but the darkening effect does not occur on those parts of it which are covered with sheets of glass.*

This fact was quite incomprehensible at the time mentioned, and I could put forward no theory to account for so very singular a result. At present it is easy to account for it, by admitting the existence of the Röntgen rays in ordinary sunlight: the white compound which darkens when exposed to sunlight is not sensitive enough to be much affected by light such as will readily affect an ordinary photographic plate; but light which contains the Röntgen rays will affect it and darken it (the dark colour produced becoming bleached again when kept in darkness). Hence I conclude that the Röntgen rays form part of light which reaches us from the Sun, and that it is these rays only which affect the white compound in question.

Perhaps, some day, other compounds will be discovered which act in the same manner towards solar light.

The Casa Mia Laboratory, Putney, S.W.
May 5, 1896.

THE ACTION OF THE RÖNTGEN RAYS UPON DOUBLE AND TRIPLE ELECTRIC STRATA.

By M. N. PILTSCHIKOFF.

SEVERAL physicists have studied the action of the Röntgen rays upon electrified metals; in other words, upon a simple electric stratum. I have also occupied myself with this question (*Comptes Rendus*, cxvii., p. 713), but I have, further, made, in concert with my assistant, M. Totchidlovsky, several experiments upon double and triple electric strata.

I have first observed that a plate of glass, of paraffin, of ebonite, mastic, &c., charged with electricity, either positive or negative, are rapidly discharged by the action of the Röntgen rays, as well if the rays fall upon the charged surface as if they traverse the plate, falling upon the neutral surface. I then undertook to study the action of the Röntgen rays on the charge of a condenser formed by a plate of paraffin (17 c.m. x 11 c.m. x 1 c.m.), of a stratum of air (1.8 m.m. in thickness), and of a disc of zinc (diameter, 10 c.m.; thickness, 3.55 m.m.). I first charge the central part of the inner surface of the paraffin plate with negative electricity, and then put the zinc disc in its place. Exner's electroscope, connected metallically with the disc, shows, e.g., -170 volts. I

touch the zinc; the free electricity is dissipated, and there only remains a double electric stratum. I cause the paraffin plate to be traversed by Röntgen rays (issuing from a window of aluminium) during one minute; no measurable loss of the double stratum is produced. I repeat the same experiment, charging the paraffin plate with positive electricity; the same result. Thus the double electric layer is only destroyed by the Röntgen rays very slowly.

If, instead of touching the zinc disc, I leave its charge intact, this charge, according to the law of electric distribution on conductors, occupies exclusively the external surface of the disc, and my condenser in this case possesses a *triple layer* of electricity. The electroscope marking a deviation corresponding to 170 volts, I cause anew the Röntgen rays to fall upon the paraffin plate. In nine seconds the electroscope falls to 85 volts, or the half of its primitive charge, showing that half the free electricity of the triple layer is dissipated in nine seconds. It is easy to demonstrate that it is exactly the free electricity of the zinc which has been dissipated. In fact, if we touch the zinc disc and convey to the earth the rest of the free electricity of this disc, the electroscope will indicate 0 volt. If, then, we take off the disc (which always remains in metallic connection with the electroscope), we observe on the electroscope an initial deviation of +170 volts.

This discharging action of the X rays through a double stratum, which remains almost intact, and through a disc of zinc, which is absolutely opaque to these rays, upon the free electricity of the outer surface of the disc, appears no less unexpected than difficult to explain.—*Comptes Rendus*, cxvii., p. 839.

ON THE RÖNTGEN RAYS ELECTRISED.

By A. LAFAY.

THE experiments on Röntgen's rays electrified which I have already had the honour of communicating to the Academy, give room for an objection which it was necessary to remove.

We may ask ourselves if these rays really undergo a change of nature, an *electrisation*, in traversing the electrified lamella, or if the deviations observed are merely the result of the combined effect of the electro-magnet and of the electric field developed by the silver plate.

To remove this uncertainty, I have repeated the experiments already described, and I have caused the electrified ray, on its issue from the lamella, and before its passage between the keepers of the electro, to penetrate into a Faraday case placed in communication with the earth. The sensitive plate was contained in the interior of the metallic case, which presented merely a small aperture destined for the entrance of the rays. In these conditions, which eliminate as far as possible the effects of the electric field, I have observed the same deviations as formerly.

In order to throw yet more light on the nature of the electrified rays, I have repeated with them the experiment which M. Perrin has performed on the cathodic rays.

In the present case, the execution of the experiment presented no difficulty. For the ball of a gold leaf electroscope I substituted a Faraday's cylinder, the aperture of which is turned upwards. The apparatus, thus transformed, is completely enclosed in a metallic cylinder, the upper opening of which is closed with a leaden cover which has a central aperture. Above this aperture I arrange a silver plate connected to a Wimshurst machine, which serves to electrify the rays sent by the Crookes tube, placed above.

In these conditions, I observed that the Faraday cylinder is charged with electricity of the same kind as that supplied to the electrifying plate. The phenomenon

continues if we substitute for silver a metal leaf of any kind sufficiently thin to be traversed by the Röntgen rays.

We still obtain the charge of the cylinder if we close the aperture in the leaden cover with a transparent dielectric (paraffin, ebonite, paper, &c.); it is no longer the same with an opaque dielectric, such as a plate of glass with a base of lead.

In view of this result, it is natural to demand if a very thin sheet of metal placed in communication with the earth would not equally allow itself to be traversed by the electrified flux, and if the conductivity of the metal would be sufficient to deprive the rays of all their electricity.

It has not yet been possible for me to satisfy myself of this fact by an experiment such as I have just described, but we must remark in the present case the radiation is weakened by its passage through the plate; and that, further, the Röntgen flux, acting as a conductor between this plate and the Faraday cylinder, increases the losses of the electroscope. This is why I purpose, by a method slightly modified, entering upon the investigation of this question, which presents a great interest, and would give the key to the remarkable results obtained by Lenard.

I shall conclude this paper by indicating a very curious fact. In my former communication I had, after the example of Hittorf, assimilated the Röntgen flux to a sheaf of flexible conductive wires. This manner of conceiving the phenomenon occasioned me to modify the experiment already described in the following manner:—

I completely enclosed the photographic plate with leaves of aluminium, then putting the platinum wire and the lead screens in communication with the earth, I have, whilst the electro-magnet was at work, electrified the metallic envelope containing the plate.

In these conditions, the hypothetical filaments of Hittorf permit the efflux of the electricity developed on the aluminium, and should, in consequence, bend in a direction determined by the action of the magnetic field.

The deviations observed have entirely confirmed this view, and I have thus verified—a result at first slightly paradoxical—that it is indifferent for deflecting the Röntgen rays to electrify them before and after their passage across the magnetic field.—*Comptes Rendus*, cxxii., p. 837.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 218).

CHAPTER XII.

THE CHARACTER IMPARTED TO FLAMES, AND TO AN ELECTRIC SPARK OR ARC, BY THALLIUM AND ITS COMPOUNDS.

The Luminous Spectra of Thallium.—It is well known that in March, 1861, Mr. Crookes, when making a spectrum analysis of a flame containing the residue of certain samples of selenium, found in the spectrum of this green flame a very bright green line. He traced the colour of the flame and the appearance of the green line to the existence of a new element, to which he gave the name thallium. On the 16th of May, 1862, the late M. Lamy proved that the element discovered by Mr. Crookes was a metal. The subsequently published works by Mr. Crookes and the late M. Lamy, on the physical and chemical properties of thallium and its compounds, are well known; I have no intention of reverting to that subject here. I will confine myself to mentioning that Messrs. Crookes and Lamy agreed in assigning a single line to the thallium spectrum. At the request of M. Lamy, Messrs. Bunsen and Kirchhoff submitted, early in 1863, the flame charged with this metal to spectroscopic analysis, and found a line which they could not split up when using the large spectroscope used by M. Kirchhoff

during his study of the solar spectrum. They assigned to this single line the number 1442.6 on the scale of M. Kirchhoff's instrument.

About the same time, the late Mr. Miller made a spectroscopic examination of thallium and its sulphate as prepared by Mr. Crookes. When introducing in succession the metal and its sulphate into a hydrogen and into an oxyhydrogen flame, he likewise found a single line.

He also found that Mr. Crookes's metal, when put into an induction spark, showed a more complex spectrum, containing lines characteristic of cadmium, zinc, and lead.

In his work published in 1874, M. Lecoq de Boisbaudran attributed a single line to the electric spectrum of thallium and its compounds; but he gave two green lines for the flame spectrum, one very brilliant, the other very faint.

M. Bunsen took up this work again about the same time. The results of his investigations are given in his "Spectral-analytische Untersuchungen." When working on most carefully purified thallous chloride, he found that the flame and electric spectra of this compound each consisted of a single line, the respective positions of which on the scale of his spectroscope he gave.

Lastly, Prof. Liveing, in his work on the ultra-violet spectra of the elements, published in 1883, gave a very complex spectrum for thallium.

These discrepancies decided me to subject the methods of obtaining pure thallium and its principal compounds to a thorough revision, with the object of ascertaining whether the differences noted were due entirely to the want of purity of the materials used by different observers, or whether they could or ought to be imputed either to the method of investigation adopted or to the analysers used.

When undertaking this research, I also wished to ascertain whether it was possible to obtain thallium and its principal compounds in such a state that, when introduced into a flame or an electric spark or arc, they would not show any trace of the sodium line, and whether it was possible, by raising the temperature, to cause the appearance of one of the lines characteristic of potassium, lithium, calcium, strontium, or barium, in the thallium spectrum.

In the last chapter the researches I undertook, for the purpose of obtaining thallium and its compounds of uniform composition, are described. I may refer chemists who wish to study those researches to that chapter; I will limit myself to describing here the spectroscopic studies of the above materials, in the order described in that chapter.

The Flame Spectrum of Sulphate of Thallium prepared by M. Lamy.—I commenced my observations by means of this sulphate, from which I had eliminated all impurities. When introduced into a pure hydrogen flame, it imparted to it a pure green tint. Spectrum analysis of a flame into which sulphate that had been purified, and then crystallised four times in succession, had been introduced, enabled me to see a single line, the well-known green thallium line. On substituting a dark blue coal-gas for a pure hydrogen flame, I found only a single line, but it lacked the intensity of colour of the thallic flame from a well-made Bunsen burner, as well as the pure tint of a thallic flame of pure hydrogen; it appeared to be a mixture of green and blue. The flame was greener in the outer layers and bluer inside.

Sulphate of thallium, when introduced on a platinum loop coated with iridium into a flame of hydrogen raised to incandescence by the admixture of oxygen,—that is, in the blue hydrogen flame,—coloured it a very much paler green than hydrogen burning with a dark flame. The same phenomenon occurred with an oxy-coal-gas flame.

When it was introduced into the inner cone of an oxyhydrogen or oxy-coal-gas flame, by means of a fine platinum wire loop coated with iridium, the thallic tint

of the flame was so weakened that it seemed to have disappeared; it was only recognisable at a distance of from 1 to 2 c.m. from the point of contact.

The spectrum of sulphate of thallium in incandescent hydrogen, or in the inner cone of an oxyhydrogen or oxy-coal-gas flame, consisted of the single green line. In incandescent hydrogen the spectrum consisted of a dark band, on which appeared the single line only.

Thallic rays mask rays from incandescent hydrogen. To ascertain the truth of this fact, it suffices to introduce sulphate of thallium into hydrogen sufficiently incandescent to show a bright continuous spectrum; at the instant of introduction the continuous spectrum is extinguished, and replaced by a dark band showing the single green line. The facts are different when sulphate is introduced into the inner cone of an oxyhydrogen or oxy-coal-gas flame, and this part of the flame is analysed. The single line is distinctly seen, but the spectrum is not dark; a continuous spectrum is seen. When there were two observers, and a third person engaged in introducing sulphate into the inner cone, they could in turn see the background of the spectrum dark, or showing a continuous spectrum with a single line, according as spectrum analysis was made of a part away from the inner cone, or of the inner cone itself. According to the conditions, therefore, the thallic rays could or could not mask the rays from incandescent hydrogen.

Rays from thallic sulphate instantly masked the hydrocarbon spectrum.

When working with thallic sulphate which did not show the sodium line when put into a pure hydrogen flame, burning in pure air, I was unable to cause the appearance of the sodium line by raising the temperature, whether I used an oxyhydrogen or oxy-coal-gas blowpipe. Besides, the experiment is very difficult, on account of the great volatility of the sulphate.

It succeeded best with pure iridium. I arranged a thick layer of this metal on a small piece of pure carbon let into a block of compressed magnesia, and which had been for some time kept at white heat in a pure carbon crucible. After heating the iridium in an oxyhydrogen blowpipe until it became soft, I gradually dropped the sulphate on to it. The thallium line alone appeared, either on a continuous spectrum or on a dark band, according to whether the thallic flame were examined near the point of support or at $1\frac{1}{2}$ to 2 c.m. from it; but in any case *neither the sodium D line nor any other line appeared.*

On introducing a small cone of pure carbon, saturated and completely covered with fused thallic sulphate, into the inner cone of an oxyhydrogen or oxy-coal-gas blowpipe, exactly the same spectrum was seen,—that is, the single green line on a bright or dark background, according to the part of the flame examined. When using the large Hilger spectrocope fitted with its six Iceland spar prisms, the dispersion of which is so great that seven lines were easily seen between D_1 and D_2 in the solar spectrum, the thallium line was not split up; this confirmed the observation made in 1863 by Messrs. Bunsen and Kirchhoff; the only change noticed, and one which always occurred, was the decided weakening of the green tint when it was examined against a bright background.

Does the impossibility of seeing the sodium line in the spectrum of thallic sulphate prove the absolute absence of sodium from the vapour submitted to spectrum analysis? The facts I have just mentioned tend to show that this question must be answered with caution. It is an undoubted fact that the thallic sulphate, before being repeatedly crystallised, showed the sodium line strongly and persistently, and that after these repeated crystallisations the sodium line could no longer be detected. It is also certain that sulphate thus freed from any quantity of sodium capable of being detected by spectrum analysis, when left in air under a bell-jar for several days, gave positive signs of the presence of sodium. Having reached this point, it is found that the colour intensity of the so-

dium line is very weak, that the thallic rays have a great influence on this colour intensity, and that they can mask, or at least render invisible, the sodium line, when they have reached a given limit. When one has succeeded in procuring a thallic sulphate which no longer shows the sodium line in hydrogen burning in pure air, and when one introduces this sulphate into a Bunsen flame burning in air, and showing the sodium line, though faintly, one notices the instant disappearance of this sodium line as soon as the thallium line appears. If the air is so much contaminated that yellow scintillations appear in flames, as is almost always the case when the air is in motion, the continuous sodium line is seen to disappear, and a weak intermittent sodium line appears. It is evident, then, that thallic rays exercise an extinguishing power over sodium rays. This power, moreover, appears definitely limited as regards sodium, but yet it is sufficient to justify a doubt as to the possibility of ascertaining whether it is possible to procure thallium or a thallic compound absolutely free from sodium.

I discuss the question in a general sense, because I found the same property in all the thallic compounds I have mentioned.

Having verified these facts, I used purified thallic sulphate to prepare metallic thallium and its trioxide and chloride.

I gave all necessary details in the last chapter, to which I refer the reader.

The Flame Spectrum of Thallium prepared from M. Lamy's Sulphate.—Thallium prepared by electrolysis this sulphate, when introduced into a hydrogen flame or a Bunsen burner, on the end of a fine platinum wire loop, burnt in them with a bright light, and coloured them the same as the sulphate from which it was reduced. Spectrum analysis only showed a single very brilliant green line. I repeated the experiment when the air contained a very sensible amount of sodium, without being able to cause the sodium line to appear on the dark background showing the green line.

Part of the same thallium, when left for three days in dry air, in a well-closed cupboard, occluded from the air enough sodium to show the sodium and thallium lines, when introduced into a hydrogen flame, until the metal was completely volatilised. In hydrogen raised to incandescence by burning in oxygen, the thallium burnt with extreme brightness. When the slit was narrow enough, the spectrum was dark, and showed the single very intense green line. If, on the other hand, the slit were wide enough to show the green line at least 1 m.m. in width, a continuous spectrum appeared between Fraunhofer's C and F lines, and the intensity of the line was greatly diminished. Owing to the bright light, *lines could easily be overlooked.* On two occasions I made spectrum analyses of an oxyhydrogen flame impinging on pure iridium heated nearly to its fusing-point, and on which I had dropped some small globules of thallium. I saw the thallium line alone on a partially continuous spectrum. I was not able to cause the appearance of the sodium or any other lines, or to split the thallium line when using the large Hilger spectrocope with its six prisms, or by means of Rutherford's grating, substituting it for the prism in the Steinheil spectrocope. I made this last experiment with the help of M. Fievez. I am convinced that it is not possible to make a trace of sodium, or at least to see the sodium line, at a temperature above the fusing-point of iridium, when the thallium experimented with does not show the sodium spectrum at a low temperature.

(To be continued).

Effects of Smoke upon Agriculture.—According to Max Hagen, the smoke of wood-fires is not in the slightest degree injurious to vegetation. — *Chemiker Zeitung.*

A REVISION OF THE ATOMIC WEIGHT OF ZINC.*

FIRST PAPER: THE ANALYSIS OF ZINCIC BROMIDE.

By THEODORE WILLIAM RICHARDS
and
ELLIOT FOLGER ROGERS.

Introduction.

In an account of a recent investigation on the occlusion of gases by the oxides of metals (*Proc. Amer. Acad.*, xxviii., 200, Richards and Rogers) it was shown that zincic oxide, in common with cupric and magnesian oxides, has the power of retaining important quantities of oxygen and nitrogen gases, even at very high temperatures. Hence it was evident that all determinations of the atomic weight of zinc depending upon the conversion of the metal into the oxide through the ignition of the nitrate must be influenced by a constant error, which has the tendency to make the results lower than the true value. In consideration of this fact, it becomes very important to review all of the results thus far obtained regarding the atomic weight of zinc, in order to determine how seriously the error in question may influence our accepted value. A chronological list† of the accepted data is given below:—

1809.	Gay-Lussac, <i>Mém. d'Arceuil</i> , ii., 174 . . .	65'55
1811.	Berzelius, <i>Pogg. Ann.</i> , viii., 184 . . .	65'57
1842.	Jacquelain, <i>Ann. de Chim. et de Phys.</i> , [3], vii., 204 . . .	66'24
1844.	Favre, <i>Ann. de Chim. et de Phys.</i> , [3], x., 163 . . .	65'99
1844.	Erdmann, <i>Berz. Jahresber.</i> , xxiv., 132; and <i>Pogg. Ann.</i> , lxii., 612 . . .	65'05
1883.	Pelouze and Fremy, "Chem.," p. 55 . . .	65'07
1883.	Baubigny, <i>Comptes Rendus</i> , xcvi., 906 . . .	65'41
1883.	Marignac, <i>Archiv. Sci. Phys. et Nat.</i> , [3], x., 5, 193 . . .	65'30
1885.	Van der Plaats, <i>Comptes Rendus</i> , c., 55 . . .	?
1887.	Reynolds and Ramsay, <i>J. Ch. Soc. Trans.</i> , li., 854 . . .	65'67
1888.	Morse and Burton, <i>Am. Chem. Journ.</i> , x., 311 . . .	65'27
1889.	Gladstone and Hibbert, <i>J. Chem. Soc. Trans.</i> , lv., 443 . . .	65'44

The various results have been reached:—

1. By converting a known weight of metallic zinc into the oxide (Berzelius, Jacquelain, Erdmann, Morse and Burton).
2. By the evolution of hydrogen from acids by metallic zinc, the hydrogen being either measured or burned (Jacquelain, Favre, Van der Plaats, Reynolds and Ramsay).
3. By the conversion of a salt of zinc into a zincic oxide through ignition (Favre, zincic oxalate; Pelouze, zincic lactate; Baubigny, zincic sulphate).
4. By the determination of the electrolytic equivalent of zinc (Gladstone and Hibbert).
5. By analysis of a haloid salt of zinc (Marignac).

The work of Morse and Burton by the first method is so far superior to the previous determinations made in the same way, that the older ones may be wholly neglected. The two or three possibilities of infinitesimal error, such as the chance that the zinc might contain impurities taken from the glass used for its distillation, may be wholly neglected when compared with the great error due to the occlusion of nitrogen and oxygen. As the amount of this error is dependent upon the physical conditions of the zincic oxide, it is impossible to make an accurate correc-

tion except by the actual determination of the gas in the oxide remaining from the determinations. From our own experiments (*Proc. Amer. Acad.*, xxviii., 200) it would appear that a grm. of zincic oxide obtained from the nitrate usually contains about 0'00057 grm. of occluded gas; upon this basis, Morse and Burton's result would become 65'458 instead of 65'269.

In considering the results obtained by the second method, the results of Favre and Jacquelain may be rejected at once. Of Van der Plaats' results it is necessary to state only that some error must have crept in while recording his data, for it is inconceivable that 6'6725 grms. of zinc should yield only 1'1424 litres of hydrogen. The work of Reynolds and Ramsay was much more careful and detailed; but the results varied very widely. Hydrogen evolved from very pure zinc was measured, with many precautions, but after the rejection of thirty-four experiments eleven more gave a value of 65'24, and still five more gave 65'47 as the atomic weight of zinc. Since the publication of their work many investigations have shown that the density of hydrogen is greater than the value assumed at that time. If a litre of the gas weighs 0'0001 grm. (Lord Rayleigh and others) and the atomic weight of hydrogen is taken as 1'0075 (O=16'000) the atomic weight of zinc deduced from Reynolds and Ramsay's experiments becomes about 65'63.

The two older results obtained by the third method are worthy of no further mention. Baubigny's work upon the ignition of zincic sulphate is very interesting, but probably incomplete. It will be remembered that the value for copper obtained by the same method was too low (Richards, *Proc. Amer. Acad.*, xxvi., 275), owing, probably, to the occlusion of sulphuric acid by the cupric sulphate. It is not impossible that a similar error may have crept in here, for the conditions are similar; but it is probable that it is here counterbalanced by the retention of sulphur trioxide by the zincic oxide. In a series of experiments made in this laboratory, pure zincic oxide obtained from the carbonate (as described further on), was ignited to constant weight in an oxidising atmosphere at a temperature above the fusing-point of gold*; it was then dissolved in dilute sulphuric acid, which left no residue upon evaporation, and very gradually brought again to the same high temperature. In no case were we able to expel all of the sulphuric acid which we had added. Three experiments are appended:—

Weight of zincic oxide before. Grm.	Weight of zincic oxide after, Grm.	Gain. Grm.
1'03009	1'03032	0'00023
0'80243	0'80265	0'00022
1'03447	1'03473	0'00026

Average for 1 grm. ZnO. . . 0'00025

Gladstone and Hibbert deposited silver in one cell by means of a voltaic current, while zinc was being dissolved from an amalgamated plate in another. Although the experiments are interesting, it would appear from the results of Vanni (*Ber. d. D. Ch. G.*, xxiv., Ref. 882) and others that the possibility of side reactions makes the strict applications of Faraday's law for the determination of atomic weights of rather doubtful efficacy. One would expect the method adopted to give a result larger than the true one.

Marignac's work upon the chloride of zinc and the double chloride of zinc and potassium is even less satisfactory than his investigations of other chlorine compounds; it merits no further notice.

It is evident from these statements that the three least unsatisfactory determinations are all vitiated to a greater or less extent by constant errors:—The work of Morse and Burton by one which tends to lower the result; the

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*. Presented April 10, 1895.

† Much assistance in preparing the list has been obtained from the works of Clarke, Meyer and Seubert, and others. The results have been re-calculated with the assumption of the following atomic weights:—O=16, C=12'002, Cl=35'456, Ag=107'93, H=1'0075.

* Four grms. of pure gold melted in fifteen minutes from the time of turning on the air blast in the furnace.

work of Gladstone and Hibbert by one which may tend to raise the result; and the work of Baubigny by two which tend to counteract one another. One would expect the atomic weight of zinc to prove in the end equal to about 65.4.

It seemed very desirable to obtain a series of determinations which should be wholly different from any of these; and for this reason zinc bromide was chosen as the starting point of the present research. Additional advantages presented by the use of this substance are the fact of its ready and accurate analysis, and the fact that a determination of the ratio $2\text{Ag} : \text{ZnBr}_2$ would bring the element into a series of elements which have been determined by Stas and others with great precision in this way.

(To be continued).

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY CONVERSAZIONE, MAY 6, 1896.

On this occasion there were submitted to the Fellows and the visitors a number of most interesting exhibits in illustration of recent discoveries.

"Röntgen's rays" formed the subject-matter of three exhibitions.

In the Officers' Room, Mr. A. A. C. SWINTON gave a practical demonstration of the "New Photography"—a name which we hope is merely provisional.

When a suitable Crookes vacuum tube is excited, the invisible radiations that proceed from the point where the cathode rays strike a solid substance, will impress photographic plates, will cause certain salts to fluoresce, and will discharge electrified bodies.

These radiations pass with ease through various substances which to ordinary light are quite opaque, while they penetrate with difficulty other substances which to light are very transparent.

Since bone is more opaque to these rays than tissue, it is possible by their means to obtain shadow pictures of the bones in the living body either upon a photographic plate or upon a fluorescent surface within a cryptoscope. Similarly other hidden objects, such as the coins in a purse, the contents of closed boxes, and such like, can be rendered apparent.

In the Council Room, Mr. SYDNEY ROWLAND gave a copious and most instructive series of "skiagrams," chiefly with reference to medical and surgical diagnosis.

The following analysis, based on a record of some fifty cases, is useful as showing the branches of surgery in which the new process will probably be found of most use. About 20 per cent of these include the discovery and location of foreign bodies, needles, bullets, &c., lodged in soft tissues, and in one case a coin lodged in the intestine, which caused troublesome symptoms. In one of these cases two previous operations had been fruitlessly performed. 15 per cent of the cases were instances of pathological conditions of the elbow joint of more or less obscurity, on which new and unexpected light was thrown by the diagnosis thus obtained. In 10 per cent of the cases the object in view was the determination of the extent and distribution of tuberculous lesions in bone. Various ankyloses and deformities of the bones and joints of the extremities have made up the remainder of the cases.

In the same room, Mr. HERBERT JACKSON demonstrated the use of phosphorescent substances in rendering the X rays (Röntgen's rays) visible.

The tube used to produce the rays is a slight modification (described in the *Proceedings of the Chemical Society*) of a tube originally introduced by Mr. Crookes to illus-

trate the heating effect of cathode rays. These are brought to a focus at the centre of curvature of the concave cathode, whence they proceed in nearly a straight line to a platinum plate, from the surface of which they are apparently scattered in all directions. The rays penetrating the glass fall upon phosphorescent bodies and are rendered visible, thus showing the different extents of response of these bodies to such rays.

Helium also took a prominent place among the exhibits. In the Principal Library, Mr. F. McCLEAN, F.R.S., exhibited photographs of the spectra of twenty-three of the most characteristic helium stars. It is noted that in 1892 Prof. Lockyer ascribed the peculiarity of the spectra of these stars to the presence of helium.

In the same room, Prof. CLOWES, D.Sc., exhibited a new method of gas-testing in electric culverts.

This apparatus is also suitable for detecting and measuring inflammable gas in inaccessible places in gas works, coal bunkers, coal mines, and furnace flues. It weighs only 11 lbs.

A standard hydrogen flame, fed from a small steel cylinder of the compressed gas, is inclosed in a brass vessel provided with a transparent front. This apparatus is mounted on a camera tripod, and is observed by throwing a black cloth over the head. The air to be tested for inflammable gas is pumped over the flame by dropping the end of a flexible tube into the culvert, and compressing a rubber ball provided with suitable valves. A constant stream of the air is thus caused to pass over the hydrogen flame, and by the appearance and dimensions of the flame-cap produced, gas is detected and its percentage is accurately measured. The hydrogen flame can be adjusted to two standard heights, and thus percentages of gas from 0.2 to 5 can be detected and measured.

In the same room, Prof. HARTLEY, F.R.S., displayed a series of photographs of spectra in illustration of the Bessemer flame, taken at the North-Eastern Steel Co.'s Works, at Middlesbrough-on-Tees.

The series show:—Four photographs of the Bessemer flame seen issuing from the converters, 15 in. by 12 in.

Two plates of spectra of the Bessemer flame, 12 in. by 10 in.

Thirteen spectra (plate 17) taken at intervals during the "blow," and also during the "over-blow." The spectra slightly overlap. This series shows the increase of temperature during the combustion of the carbon. A gallium line is seen in ten of the spectra.

The detection of gallium in the Bessemer flame spectra (plate 24).

Three plates of spectra, 12 in. by 10 in., illustrating the method of detecting gallium by spectrum analysis of substances separated from the metal and ore.

Plate 51, showing—(1) Spectrum of sesquioxide metals separated from 1 kilo. of Cleveland iron ore. (2) The spectrum of an insoluble residue collected on a filter-paper and burnt. (3) Precipitate from the solution of a manganese ore collected on a filter and burnt. It contains indium. Plates 53 and 54 are of a similar description.

Prof. LIVERSIDGE, F.R.S., showed gold nuggets displaying their internal structure. The specimens (Australian) had been sliced and polished, and were then etched with chlorine-water, thus showing the internal crystalline structure and the enclosures of quartz, iron oxide, &c.

In the Secretaries' Room, the Gas Cylinder Committee exhibited the results of experiments on steel gas-cylinders.

These show—(1) The danger of using hard or unannealed steel for gas cylinders; (2) the extraordinary amount of violent ill-treatment to which a good soft annealed cylinder may be subjected without destruction, even when charged to 120 atmospheres; (3) the effect of very great internal pressure steadily applied, in this case due to the expansion of liquefied ammonia gas which

completely filled the cylinder when cold; (4) the violently destructive character of the explosion of mixed gases under pressure which no practicable cylinder can withstand.

Prof. WORTHINGTON, F.R.S., and Mr. R. S. COLE exhibited instantaneous photographs of splashes.

These photographs were taken each with an electric spark giving an exposure of less than 3-millionths of a second. The spark could be so timed as to pick out any desired stage of the splash within limits of error not exceeding, as a rule, about 2-thousandths of a second. In this way the progress of a great variety of splashes has been followed in minute detail. Specially interesting are those which illustrate the formation of a bubble, and those which show how the nature of the disturbance produced by the entry of a solid sphere depends on the condition of its surface. The motions set up even by a smooth sphere are difficult of explanation.

Prof. ROBERTS-AUSTEN, C.B., F.R.S., showed modifications of an experiment of M. Charles Margot by Professor Roberts-Austen, C.B.

A wire of aluminium is raised, by a current of 30 amperes, to a temperature far above the melting-point of aluminium, but a film of oxide on its surface prevents the wire from breaking. The molten wire through which a current is passing, may then be attracted by a magnet.

Mr. J. NORMAN LOCKYER, C.B., F.R.S., exhibited—
1. Flint glass prism of 9 inches aperture and 45° refracting angle.—The prism has been constructed by the Brothers Henry, of the Paris Observatory, and will be used as an objective prism for photographing the spectra of stars.

2. Photograph showing positions of coronal spectrum rings in the total eclipse of the sun, April 16th, 1893.—The original negative was taken by Mr. Fowler, at Fundium, West Africa, with the 6-inch prismatic camera near the middle of totality, with an exposure of forty seconds. In addition to the images of a number of prominences, there are portions of rings representing the radiation spectrum of the corona. The brightest of the rings corresponds to the well-known corona line 1474 K, but the others have not been previously photographed. All the rings are most intense in the brightest coronal regions, near the sun's equator.

3. Photographic spectra of α Cygni, γ Cygni, and Arcturus.—The photographs were taken at South Kensington with a 6-inch objective prism of 45°, and illustrate the difference between stars of increasing and stars of decreasing temperature. Arcturus is a cooling star, almost identical with the sun, while α Cygni differs very widely from the sun and is getting hotter. The spectrum of γ Cygni, like that of Arcturus, consists of a very large number of lines, but as many of the more prominent lines agree with those of α Cygni, and are absent from the solar spectrum, this star must be classed with those of increasing temperature.

4. Photographs showing the spectra of helium and gas X in relation to the spectra of Orion stars.—The lines of the two gases are arranged in the series deduced by Messrs. Runge and Paschen, and their distributions in the spectra of Bellatrix, Rigel, δ Orionis, and Spica are shown.

5. Photographic map of the spectra of metals of the iron group.—The map extends from wave-length 3900 to 5900, and includes the spectra of iron, manganese, cobalt, nickel, chromium, and uranium, as shown at the temperature of the electric arc. Rowland's map of the solar spectrum forms the term of comparison, so that the wave-lengths of the lines can be read off directly from the map.

In the Meeting Room, Prof. MELDOLA, F.R.S., exhibited, on behalf of Prof. Lippmann, a series of colour photographs by the interferential method.

And at 11 o'clock Prof. DEWAR, F.R.S., showed some brilliant experiments with liquefied air and oxygen.

CHEMICAL SOCIETY.

Ordinary Meeting, April 23rd, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. J. W. Helps, B. Bernard Turner, C. Edward Sage, were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Robert Addie, Langloan Iron Works, Coatbridge, N.B.; Samuel William Allworthy, M.A., 32, Lonsdale Terrace, Belfast; John Caley, 41, Norfolk Street, Beverley Road, Hull; Charles Matthew Crossman, B.Sc., 23, Euston Buildings, N.W.; Ralph Hamilton Hanger, Riverslea, Stoneferry, Hull; William Arthur Finch Lethbridge, Ivy Cottage, St. David's, Exeter; Cecil Rudolf Lidgey, 43, Marmora Road, Honor Oak, S.E.; William McConnell, jun., 25, Percy Gardens, Tynemouth; James Stanley Muir, 27, Huntley Gardens, Glasgow; James Haddon Overton, 15, West Street, Banbury; Hastings Montagu Page, Poona; Arthur Payne, 12, Victoria Square, Newcastle-on-Tyne; George Egerton Scott Smith, 67, Surrey Street, Sheffield.

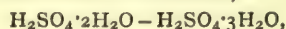
Of the following papers those marked * were read:—

*51. "The Constitution of the Cereal Celluloses." By C. F. CROSS, E. J. BEVAN, and CLAUD SMITH.

The general bearings of the subject, of which this is a special part, have been dealt with in previous communications (*Trans.*, lxx., 472; lxxvii., 433; *Ber.*, 1893, 2520; 1894, 1061; 1895, 1940 and 2604; *J. Amer. Chem. Soc.*, 1896, 8).

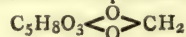
It is now shown that the cereal celluloses may be resolved by acids into soluble derivatives of their fufuroid constituents, leaving a residue of a normal cellulose, and a process has been devised which sharply effects this separation.

Two methods of hydrolysis have been studied:—
(1) treatment with acids of the series,—



in the cold, dilution and filtration from re-precipitated cellulose, the fufuroid remaining in solution; (2) treatment with dilute sulphuric acid, 1 to 2 per cent strength, at 1 to 9 atmos. steam pressure. The best results are obtained on short heating (15 mins.) at 3 atmos. The fufuroid is then obtained quantitatively.

From a study of composition, cupric reduction, yields of fufural, yields, composition, and properties of osazones, and certain special oxidations, it is concluded that the fufuroid in question is a pentose monoformal,—

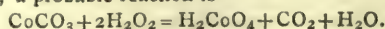


Such a compound, having the empirical formula of a normal cellulose, could arise within a cellulose complex by transformation of the terminal, CH_2OH , of a hexose molecule; i. e., an oxidation by internal re-arrangement. The formaldehyde residue thus produced is not split off, but remains united by oxygen with the pentose residue which is simultaneously produced.

*52. "On a New Compound of Cobalt, and a Rapid Method of detecting Cobalt in presence of Nickel." By R. G. DURRANT.

The author shows that if excess of sodium or potassium bicarbonate is added to a solution of any salt of cobalt, and then hydrogen peroxide, a green liquid is formed.

This liquid appears to contain a cobaltate or cobaltic acid, H_2CoO_4 , for, although the substance has not at present been isolated, volumetric determinations show that the maximum green colour is reached when the molecular proportions of the cobalt salt and hydrogen peroxide are as 1 : 2; a probable reaction is—



The green solution may be formed in presence of nickel salts, and the reaction serves as a ready method both of detecting cobalt, even in presence of large excess of

nickel, and of detecting nickel in presence of considerable excess of cobalt.

*53. "Ethereal Salts of optically active Malic and Lactic Acids." By THOMAS PURDIE, F.R.S., and SIDNEY WILLIAMSON, Ph.D.

J. Wallace Walker (*Trans.*, 1895, lxvii., 914) has shown that the rotations of the ethereal salts of active lactic acid are much greater when prepared by the action of alkyl iodide on silver lactate than by the direct action of acid on alcohol in presence of a mineral acid. To see if the same holds good in the cases of the other oxy-acids, the authors have prepared the ethereal salts of malic acid through the silver salt, and have compared the rotations of the salts thus obtained with the rotations of the same salts prepared from the alcohol. In every case the salts prepared from the silver salt were found to have the higher rotation.

The same result was evident on comparing the rotation of ethylic lactate prepared by the different methods. On the other hand, ethylic acetylmalates, prepared by the two methods, were found to have nearly the same rotation. A similar result was observed in the case of ethylic acetylalate.

The ethereal salts of both malic and lactic acids prepared from the alcohols were examined for racemoid compounds, but the quantity found was not sufficient to account for the low activity; this, coupled with the fact of the constancy of the activity of the ethereal salts prepared with the aid of mineral acids by various observers, and the similarity in rotation of the acetyl compounds from ethers from both sources, lead the authors to think that some other explanation of the difference of activity of the ethereal salts prepared by the two methods must be found than the supposition that the mineral acids cause racemisation.

In examining dextro-ethylic chloropropionate prepared from lævo-ethylic lactate for the presence of racemised salt by converting it into zinc lactate, it was found that the optical activity of the recovered salt was opposite to that of the zinc lactate from which the chloropropionate was derived. The active lactic acid had undergone inversion by the action of phosphorus pentachloride, as Walden (*Ber.*, 1896, xxix., 133) has recently noticed in the case of the malic acids.

*54. "Metadichlorobenzene." By FREDERICK D. CHATTAWAY and R. C. T. EVANS.

Metadichlorobenzene, although well known, is extremely costly and difficult to procure, and no directions for preparing it in quantity are available. The authors, having required large quantities of this compound for an investigation of some derivatives of benzene, have worked out a simple and very satisfactory method for obtaining it easily in bulk.

Acetanilide, dissolved in hot acetic acid, is treated with a thin paste of bleaching powder until two hydrogen atoms, occupying the meta-positions with respect to one another, are replaced successively by chlorine and a heavy liquid addition product of hypochlorous acid, and the 1:3:4-dichloroacetanilide is formed. On cooling, this sinks, is readily separated, and when treated with hot alcohol rapidly decomposes, 1:3:4-dichloroacetanilide crystallising out. The dichloroacetanilide is then heated with strong sulphuric acid, which hydrolyses it, and on pouring the solution over ice 1:3:4-dichloroaniline separates. The dichloroaniline, dissolved in a large quantity of alcohol, is then mixed with an excess of hydrochloric acid and diazotised by sodium nitrite, when, as the temperature rises from the reaction, the diazo-group first formed is replaced by hydrogen.

The yield of 1:3:4-dichloroaniline is nearly quantitative, and that of the metadichlorobenzene over 50 per cent of the weight of acetanilide taken.

*55. "On the Temperature of certain Flames." By W. N. HARTLEY, F.R.S.

The author, having for many years past studied the

nature of flames and the spectra they emit, found no practicable means of measuring their temperature, owing to the disproportionate size of the measuring instrument (a thermo-electric couple for instance), compared with the effective volume of the flame. He measured the temperature of flames by means of gold-leaf and with fine wires of platinum 1/3000 in. diameter, such as were drawn by Wollaston and used by Faraday, also with pure platinum wire 1/1000 in. thick. He furnishes evidence of the high temperature of a candle-flame, not only from the melting of gold and of platinum in the flame, but by an examination of the spectrum to be seen in the mantle. Experiments made with platinum wires heated in a bat's-wing gas flame are described, which proved that the carbon does not lower the melting-point of the platinum, at any rate in any appreciable degree. A small carbon monoxide flame melts platinum wire 1/1000 in. in thickness, and a cyanogen flame was shown to be intensely hot, for it melted such wire with extreme ease. The author believes that his experiments have dissipated the doubt that was cast on Professor Smithells' statement of the high temperature of the mantle of the Bunsen flame, and confirm his own estimate of the high temperature of the Bessemer flame.

*56. "The Determination of the Composition of a White Sou by a method of Spectrographic Analysis." By W. N. HARTLEY, F.R.S.

It is not long since, among current coin in France, there were sous of a peculiar golden-yellow colour, which were termed "white." It was supposed that they were made during the French Revolution of 1798 from any metal which could be readily appropriated, and great doubt expressed as to their composition.

To analyse the coin without injury, the method of photographing its spectrum was resorted to. The metals present being first ascertained, their relative proportions were subsequently arrived at by comparing the photograph with a series of quantitative spectra, in which solutions of known strengths yield spectra with a certain number of lines of definite length and strength. When the composition of the coin within certain limits had been thus ascertained, alloys were made to imitate the metal, and photographs of these were taken.

The third trial produced an alloy, the spark spectrum of which yielded a photograph identical with that of the coin, and its composition was found by the usual methods of analysis to be—

Lead	13.93 per cent.
Copper	72.35 "
Iron	0.85 "
Zinc	12.70 "

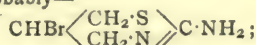
99.83

The alloy is thus seen to be a kind of brass, in which lead takes the place of about one-half the zinc. It is also richer in copper. The coin does not ring, and its edges show signs of being cracked, which may be readily accounted for by the large proportion of lead which enters into its composition.

By the method of analysis here described, it may be advantageous and interesting to determine the composition of antique jewellery and coins, as no injury results from the action of the spark.

*57. "Halogen additive Products of substituted Thiosinnamines." By AUGUSTUS E. DIXON, M.D.

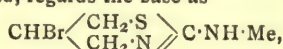
It has been recently shown by the author (*Trans.*, 1896, lxix., 17) that the "thiosinnamine dibromide" obtained by Maly (*Zeit. f. Chem.*, 1867, 42) from bromine and allylthiourea is the hydrobromide of a penthiazoline derivative, probably—



and is, moreover, identical with the substance produced by combining dibromopropylthiocarbimide with ammonia,

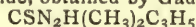
This thiocarbimide unites readily with primary and secondary amines, yielding analogous compounds. The author has lately been engaged in experiments on the production of these compounds from bromine and substituted allylic thiocarbimides. Only the phenyl and orthotolyl derivatives had been tried, the former unsuccessfully, when an abstract appeared, in the last issue of the Society's Journal, of a paper by Gadamer (*Arch. Pharm.*, ccxxxiii., 646), showing that the addition compounds can be satisfactorily obtained from substituted allylic thiocarbimides (thiosinnamines) containing fatty (methyl) groups.

An examination of Gadamer's "methylallylthiocarbimide dibromide," $C_5H_{10}N_2S.Br_2$, shows it to be saline in nature; it is, in fact, the hydrobromide of a base ($C_5H_9N_2SBr$), which is liberated on treatment of the aqueous solution with dilute alkali. The same compound, $C_5H_9N_2SBr.HBr$, is formed by mixing alcoholic solutions of dibromopropylthiocarbimide and methylamine; the author, therefore, on the grounds set forth in the paper first mentioned, regards the base as—

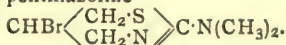


μ -methyl- γ -bromopenthiiazoline.

By analogy, it is suggested that the dimethylallylthiocarbimide dibromide, obtained by Gadamer from—



and bromine, is probably also the hydrobromide of a dimethylated penthiiazoline—

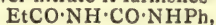


58. "Acidic Thiocarbimides, Thioureas, and Ureas." By AUGUSTUS E. DIXON, M.D.

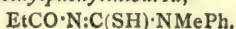
The method of preparing acidylthiocarbimides by heating the corresponding acid chlorides, dissolved in anhydrous benzene, with lead thiocyanate (Dixon and Doran, *Trans.*, 1895, 565; Dixon, *ibid.*, 1904), has now been applied to the chlorides of propionic, isobutyric, and phenylacetic acids, the yields of dissolved thiocarbimide so obtained varying from 90 per cent of the theoretical to a nearly quantitative amount. The products are pale yellowish in colour, have a characteristic, pungent, and tear-exciting odour, and are decomposed by heating with water, with formation of thiocyanic acid; they give the ordinary thiocarbimide reaction (desulphurisation) when warmed with ammoniacal silver or alkaline lead solution, and unite spontaneously with primary and secondary amines, yielding acid substituted thiocarbimides or thioureas; the former dissolve readily in dilute caustic alkali, exchanging the acid radicle for hydrogen. When treated in boiling alcoholic solution with silver nitrate, they exchange sulphur for oxygen, thereby affording the corresponding (acidic) ureas.

The following substances are described:—

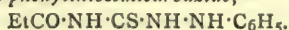
ab-Propionylphenylthiocarbimide, $EtCO \cdot NH \cdot CS \cdot NHPH$.—Brilliant, colourless prisms, m. p. 129–130°, undecomposed. With silver nitrate it furnishes—



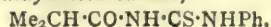
identical with the compound obtained by Kühn (*Ber.*, xvii., 2881) from phenylisocyanate and propionamide. ab-Propionylorthotolylthiocarbimide.—Hair-like needles, m. p. 143–144°. ab-Propionylmetatolylthiocarbimide.—Long, vitreous prisms, m. p. 86–87°. ab-Propionylparatolylthiocarbimide.—White needles, m. p. 127.5–128.5°. n-Propionyl-v-methylphenylthiourea,—



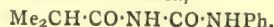
Large, vitreous prisms, m. p. 68–69°. n-Propionyl-v-phenylbenzylthiourea.—Thick prisms, m. p. 102–103°. a-Propionyl- β -phenylthiosemicarbazide,—



Obtained from propionylthiocarbimide and phenylhydrazine; tufts of brilliant white prisms, m. p. 155–156°. ab-Isobutyrylphenylthiocarbimide,—

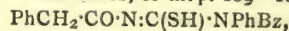


—Large, colourless prisms, m. p. 128.5–129.5°. With silver nitrate it affords the urea,—



identical with that obtained by Pinner (*Imidoäther*, 124, from butenyldiphenylthiourea and acetic acid. ab-Isobutyrylorthotolylthiocarbimide.—Short, white needles, m. p. 136–137°. The urea, $Me_2CH \cdot CO \cdot NH \cdot CO \cdot NH \cdot To$, forms long, flexible, satiny needles, melting at 134–135°. ab-Isobutyrylparatolylthiocarbimide.—Large, ice-like prisms, m. p. 134–135°. The urea crystallises from alcohol in shining needles, melting at 137–138°. ab-Isobutyryl β -phenylthiourea.—Fine needles, m. p. 167.5–168.5°.

Phenacetylthiocarbimide, $PhCH_2 \cdot CO \cdot NCS$, has a feeble odour, and attacks the eyes only slightly. By combination with aniline it affords $PhCH_2 \cdot CO \cdot NH \cdot CS \cdot NHPH$. ab-Phenacetylphenylthiocarbimide.—Lustrous, white prisms, m. p. 109–110°. The corresponding urea forms thin, white needles, melting at 168–169°. ab-Phenacetylorthotolylthiocarbimide.—Vitreous prisms, m. p. 149–150°. With nitrate of silver it gives the urea; silky, flexible needles, m. p. 161.5–162°. ab-Phenacetylparatolylthiocarbimide crystallises from alcohol in brilliant, rhombic plates, melting at 150–151°. The urea occurs in hair-like needles, of m. p. 189–189.5°.—



n-Phenacetyl-v-phenylbenzylthiourea.—Microscopic prisms, m. p. 127.5–128.5°.

All the compounds enumerated above are insoluble, or nearly so, in water; the disubstituted thiocarbimides are all desulphurised by warming with alkaline lead tartrate, or by ammoniacal silver nitrate in the cold; the trisubstitution derivatives, on the contrary, do not give up their sulphur under these conditions.

Attempts made to obtain from picryl chloride, using either lead or mercuric thiocyanate, the corresponding picrylthiocarbimide, $C_6H_2(NO_2)_3 \cdot NCS$ were unsuccessful. Experiments on the chlorides of phenylsulphonic and ethylsulphuric acids are now in progress.

59. "Apparatus for the Detection of Boric Acid." By W. M. DOHERTY, Government Laboratory, New South Wales.

The milk, wine, or other substance is made slightly alkaline with sodium carbonate, and after drying, it is thoroughly charred, not burned to an ash. The charred mass is extracted with boiling water, and the solution obtained made acid with hydrochloric acid, and evaporated gently over the water-bath in a small porcelain boat, which is placed in an apparatus of the following description:—

A piece of glass tubing, about 9 inches long and $\frac{1}{4}$ inch in diameter, is turned over at right-angles at one end and drawn to a fine aperture. A second piece of tubing about 2 $\frac{1}{2}$ inches long and $\frac{1}{2}$ inch in bore is provided with a hole in the side, and placed over the aperture and arranged so as to form a glass Bunsen burner.

The porcelain boat or other vessel containing the properly prepared substance, supposed to contain the boric acid, is placed in the larger tube, which is attached at the wide end to the gas supply, the whole being supported by a clamp. The gas is regulated so as to produce a clear flame about $\frac{1}{4}$ inch long, and free from luminosity at the extremity of the upright tube. The vicinity of the porcelain boat is heated by an ordinary Bunsen burner, and if boric acid be present, even in the most minute quantity, the small flame will show it distinctly. It will be found desirable to apply the heat gently, increasing it slowly, and carefully observing the flame in the meantime.

Lothar Meyer Memorial Lecture.

The Lothar Meyer Memorial Lecture will be delivered by Professor P. Phillips Bedson, D.Sc., at an extra meeting of the Society, on Thursday, May 28, at 8 p.m.

NOTICES OF BOOKS.

The True Atomic Weights of the Chemical Elements and the Unity of Matter. By GUSTAVUS DETLEF HINRICHS, M.D., LL.D. St. Louis, Mo., U.S.: Carl Gustav Hinrichs. New York: B. Westermann and Co.

THE key to the whole of this remarkable book is to be found in a sentence quoted on page 54 by the author, as having been used by him in a conversation with his Professor, in his early student days:—"It must be possible! It ought to be made possible!"

The apparent object of the book is to show that the atomic weights of the elements are exact multiples of half the atomic weight of hydrogen, or of a common substance which he calls "pantogen," and that the work of chemists on this subject for the past fifty years, and in particular the work of Stas, is to be summed up as "rubbish of a spurious accuracy and imaginary analysis."

The book is divided into three parts. Part I. deals with the present system of atomic weights, or, as it is termed, "The School of Stas."

Part II. is chiefly occupied with an exposition of the author's "limit method" of determining the exact atomic weights.

Part III. professes to deal with the composition of the chemical elements and the unity of matter.

We propose to consider in detail some of the points brought forward; but, before doing so, think it would be well to touch a little upon the general character of the work as a whole,—and "right here," to use one of the author's favourite expressions, we must say that for absence of the commonest courtesy to men who are deservedly recognised as leaders in chemistry, we have never seen the like!

The author, in his desire to make his theory possible, sets to work to tear down and trample upon the work of all those chemists whose researches point to the conclusion that the true atomic weights of the elements cannot be referred to half atoms of hydrogen. The work of Stas appears to particularly irritate the author, probably because of the very thorough manner in which it was carried out, and it comes in for an amount of abuse that is really amusing when one considers the relative values of the two men deduced from the work that they have done! Unfortunately Stas is dead; but if he were alive his criticism of Prof. Hinrichs would be lively reading. As for the part that Lothar Meyer and Mendeleeff have taken in the periodic classification of the elements, the former is accused of plagiarism and the latter of vain vapourism. It is in this spirit that the author makes a cool critical examination of the progress of chemistry for the past fifty years!

In Part II. the work of Dumas is considered with especial reference to the determination of the atomic weight of carbon by the combustion of the diamond, and it is here "insisted" that Stas was nothing but assistant to Dumas in that research, and had no part in the real scientific work accomplished by Dumas. How this information is arrived at is not very clear, especially when it is recorded a few pages further on that Dumas included the name of Stas in the title of this very research! But granting for the moment that it was so, what better schooling could he have had, and what could better have fitted him for the work to which he devoted his life? On page 30 the special characteristic of Stas's determinations of atomic weights in the use of large quantities of material is touched upon, and the author appears to regard the object of this method as being simply to impress the chemical world with Stas's extraordinary manipulative skill, and he appears to be unable to see that the real object that Stas had in view was to get nearer to the truth.

In the fact that in 1865 Stas gave as the value for nitrogen 14.044, and then after seventeen years' work he

was able to give—in 1882—as a closer approximation the figures $N=14.055$, the author can see nothing but what he is pleased to call "sleight of hand." Following Stas, Ostwald, Clark, Stebeleen, Van der Plaats, Thomsen, and Lothar Meyer, each come in for a full share of criticism (?) of the same order, apparently because they are unable to accept the hypothesis of Prout as consistent with experimental fact.

We next come to a "critical examination of Stas." We only purpose to select one example, and leave our readers to judge from it the value of the remainder. Stas, in his synthesis of silver nitrate, gives two values—one for the "dried" and another for the "fused" nitrate. On page 86 a quotation is given from a private letter sent by Stas to Van der Plaats, in which Stas states that the dried salt is the true nitrate, because "by fusion a slight decomposition takes place." On the very next page the author affirms that "The only legitimate conclusion that can be drawn from these experiments is that chemical compounds do not contain the elements in fixed proportions; for the amount of silver nitrate from a given weight of silver varies continuously and regularly with the absolute weight of silver employed, . . . and is constantly larger for the dried nitrate than for the same chemical compound when it has been fused."

Part II. introduces the limit method for determining the true atomic weights. Starting with the assumption that the atomic weight of every element must be a simple multiple of half the atomic weight of hydrogen, the author evidently selects the table of latest determinations and sweeps away all departures from round numbers as "spurious accuracy," so arriving at what he calls the common atomic weights of the elements. Taking this series as standard, he tabulates the results of various observers, Stas in particular, and finds that in a general way, as the quantity of material used in each individual experiment increases, the departure from the common atomic weight also increases, and that the departure from unity—H being taken as 2—is as the sum of the weights of material used in the determinations.

In this truly original manner the conclusion is arrived at that the determination of the dissociation of potassium chlorate by Penny, in 1839, who operated upon 5 grms. of material, is nearer to the truth than that of Stas, in 1860, who used 100 grms. Hence to determine the true atomic weight of any element, all that is required is to make a series of determinations under the same conditions, using the same materials, differing only in the amount taken, plot the results in a curve having as abscissa the weights of material taken and the analytical ratio as ordinates, then continue the curve so as to cut the ordinate axis,—and this point will be the true atomic ratio. It seems delightfully simple, but the whole theory rests upon the assumption that the only effect of increasing the weight of material used in a determination is to recede from the true value by the introduction of foreign matter—an assumption that is scarcely likely to be generally admitted.

The author seems to feel the weakness of the situation, and on page 183 we note a very ingenious attempt to introduce Dumas as a kind of support. A quotation from the work of that illustrious *savant*, on the Dissociation of Iceland Spar, is given. "To verify their accuracy (the atomic weights) . . . we must make analysis or synthesis on a large scale." "If," says Prof. Hinrichs, "instead of 'large scale' we say a series of increasing amounts of matter, this word of Dumas may be taken to-day as the safest guide to obtain the true atomic weights."

In Chapter III., "A Rational System of Atomic Weights," the author considers that as a standard of matter both gases and liquids are inadmissible, and proposes to reject H or O, and to take carbon in the form of diamond with an at. wt. = 12 as a standard, and as a unit exactly one-twelfth of this.

The work of Dumas is again quoted in connection with

the atomic weights of oxygen, hydrogen, and calcium, and, after the application of the favourite method of sweeping away all small departures, these elements are expressed as whole numbers.

In Part III., following this chapter, Mr. Hinrichs gives some interesting modern alchemy on the question of the possibility of the transmutation of lead and tin into gold. A rather startling piece of logic is found here. As it was held impossible to produce artificially the crystalline form of carbon known as diamond, and this supposed impossibility has now been proved to be fallacious, nothing should be looked upon as impossible, even to the manufacture of gold from the proper quantities of lead and tin! And the prediction is made that, in the hands of a Moissan of the twentieth century, "the autoclave charged with base metals may yield pure gold."

It is scarcely worth while to follow the author much further. In fact Vol. I. properly ends here, the Supplement which follows deals with the classification of the elements and a sketch of the Periodic Law. This is said to have been introduced by Lothar Meyer and Mendeleeff, and it is said of it that "so far as it was new it is not true, and so far as it is true it was not new." It is intimated that Lothar Meyer really got the idea from one of the author's papers, and then published it as his own. Mendeleeff is severely handled, chiefly on account of his predictions of elements; his periodic classification of the elements is given on page 246, and each class is taken in detail, and the mistakes and errors explained in choice language. As an example, Row 9 is said to be "indeed a chimera, the vain vapouring of an empty empiric brain."

The book now concludes with a kind of dramatic sketch, in which the possessor of truth—presumably the author—poses as a victim who is struck down and robbed by a highwayman, who, after having silenced him as he supposed for ever, publishes as his own as much of his victim's book as his "limited capacity can comprehend" under the high-sounding title of "The Periodic Law."

We have gone much more fully into this work than we should have done had not the author taken the trouble to suggest to us that our criticism, published some years ago, of his "Programme of Atom Mechanics," was written without our having read the work. In the present case, as in the former, although a few quotations here and there would have been amply sufficient, we have gone carefully through the book, and we must confess that the task was not a pleasant one. In reviewing the work of chemists for the past fifty years there are undoubtedly many instances to be found of faulty observations, hasty conclusions, and accidental errors. No man's work is perfect, and it is only by the painstaking elimination of errors discovered by experimental work that we can hope to get nearer to the goal of all true investigators, TRUTH. It would be well if at least those who occupy the position of teachers would keep this in mind, for it has been well said, by one of our most successful physicists, "There can be no great harm in a student taking an erroneous view; but when great minds err, the world must pay dearly for their mistakes."

The grand hypothesis of the unity of matter is coming more and more prominently before us every year, but we believe that that truth will be demonstrated by patient and laborious work in the laboratory, gaining here a little and there a little; work such as the classical researches of Stas furnish a luminous example. Normally, truth is gained as the result of experiment, and we cannot too strongly denounce the system that first conceives an idea, and then sets to work to make experimental data agree with it. We have faith in the unity of matter, but we believe also that the demonstration of it is more likely to be found in the work of the painstaking follower of true research than upon the "black walnut blackboard one metre square" that has been in use by the author of "Atom Mechanics" for nearly thirty years.

CORRESPONDENCE.

THE RÖNTGEN RAYS.

To the Editor of the Chemical News.

SIR,—With reference to the "Action of X Rays upon Electrified Bodies" (CHEM. NEWS, vol. lxxiii., p. 211), I have found in every case that, immediately the tube is excited, the gold leaves of the electroscope at once diverge, touch the sides, collapse, diverge again, and so on, as long as the tube is at work. The charge seems to be negative. While upon the subject of X rays, as I have seen no mention of the following fact I should like to suggest that, in the use of fluorescent screens of potassium platinocyanide, it is a great advantage to add a small quantity of calcium chloride. The addition of a deliquescent salt keeps the fluorescent material in a condition best suited to good results.—I am, &c.,

F. I. REID.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 16, April 20, 1896.

Extraction of the Terpenic Alcohols contained in Essential Oils.—A. Hailer.—The recent publication by Tiemann and Krieger on a "Method of Purifying Alcohols," specially applied to the alcohols contained in essences, compels us to make known the researches which we have for some time been conducting in the same direction. In our study on the borneols, and in particular on the camphor of rosemary, we have since 1889 utilised the property of bibasic acids for yielding with alcohols acid ethers, soluble and saponifiable by alkalis, for separating borneol from camphor. Our researches apply to different varieties of essences of geranium and citronella, of American mint, and of spike.

The Diffraction of Röntgen's Rays.—L. Calmette and G. T. L'Huillier.—Already inserted.

Observations on a Communication by MM. Benoist and Hermuzescu.—Auguste Righi.

Photography in the Interior of the Crookes Tube.—G. de Metz.—The author has obtained a dozen photographs. It seems that the cathodic rays in the interior of the Crookes tube have one of the properties of the Röntgen rays, since they penetrate aluminium, pasteboard, sensitive paper, and films, but they are stopped by platinum (0.32 m.m.) and copper (1.26 m.m.). M. Poincaré added some observations questioning that the cathodic rays possess the essential properties of the Röntgen rays.

Rotatory Dispersion of Liquids, not Polymerised.—Ph. A. Guye and Ch. Jordan.—The author concludes that—1. Active liquids, not polymerised, present only the phenomenon of normal rotatory dispersion. 2. The coefficient of dispersion in the violet, being arranged according to increasing values, it is not the same for all the other coefficients; each active body follows its own especial law of rotatory dispersion. 3. The usual rotatory powers $[\alpha]_D$ being arranged in their absolutely increasing values, the coefficients of dispersion in the violet have no—even approximate—proportionality with the rotatory powers. 4. The specific rotatory dispersions, without being proportional to the rotatory powers $[\alpha]_D$, nevertheless increase generally at the same time as the latter, the bodies with a strong rotatory power having a strong specific dispersion, and inversely; the specific dispersions are nevertheless sometimes greater and sometimes smaller

than the usual rotatory powers; the specific dispersion is therefore a constant characteristic of a chemical compound as well as the usual rotatory power. 5. There is no simple relation between the refrangibility of different radiations and the rotatory dispersions.

New Series of Sulphophosphides.—M. Ferrand.—The author has obtained, by Friedel's method, a second series of sulphophosphides, the thiophosphates, P_2S , M'_4 , i.e., those of copper, iron, silver, nickel, chromium, zinc, cadmium, mercury, lead, and aluminium.

Influence of Induction Currents on the Orientation of Living Bacteria.—L. Lorlet.—Living bacteria, in the state of motile bacilli, are very sensitive to the influence of induction currents, and arrange themselves immediately in the direction of the current. As soon as an anti-septic liquid has rendered them motionless, or has caused them to perish, the influence of electricity is annulled.

MISCELLANEOUS.

Action of the Cyanacetates of Sodid Propyl, Butyl, and Amyl upon Diazobenzene Chloride.—G. Favrel. The cyanacetates of propyl, butyl, and amyl are apt, like their lower homologues, to form hydrazones or azo-derivatives by reacting on the diazobenzene chloride, and to produce, like to them, two isomeric modifications. —*Comptes Rendus*, cxii., No. 15.

Detection of Argon in Gases issuing from the Earth.—R. Nasini and F. Anderlini.—In the gases which issue in abundance from the hot springs of Abano, and which contain CO_2 10 per cent, H_2S 1·13 per cent, CH_4 12 per cent, and N 75·7 per cent, the authors could not detect any quantity of argon worth mention.—*Gazzetta Chimica*.

Facts concerning Argon.—R. Nasini and F. Anderlini.—The authors, in their endeavour to trace atmospheric argon to the origin which they suggested in the first place in nitrogenous gases escaping from the interior of the earth, have also attempted to separate argon from the air. In so doing they have always found decidedly less in the gaseous residue not absorbed by magnesium than Lord Rayleigh and Prof. Ramsay. They observed that when the gaseous residues were passed over a fresh portion of magnesium a further portion of the gases was absorbed. Further, the noteworthy fact was observed that such gaseous residues first yielded in Geissler tubes the nitrogen spectrum, which then passed into the brilliant spectrum of argon. But after a longer or shorter time this always again disappeared and gave place anew to the nitrogen spectrum. But soon this also ceased, and at the same time the passage of the discharge through the Geissler tube. This phenomenon was observed quite invariably in all the specimens examined, showing that the argon under the influence of heat is in some manner absorbed in the Geissler tubes.—*Gazzetta Chimica* and *Berichte*.

MEETINGS FOR THE WEEK.

- MONDAY, 18th.—Society of Arts, 8. (Cantor Lectures). "Applied Electro-Chemistry," by James Swinburne.
Medical, 8.30. (Annual Oration).
TUESDAY, 19th.—Royal Institution, 3. "Ripples in Air and on Water," by C. V. Boys, F.R.S.
— Institute of Civil Engineers, 8.
— Photographic, 8.
— Pathological, 8.30. (Anniversary).
— Society of Arts, 8. "Bronze Casting in Europe," by George Simonds.
WEDNESDAY, 20th.—Society of Arts, 8. "Orthochromatic Photography," by Capt. W. de W. Abney, F.R.S.
— Meteorological, 7.30.
— Microscopical, 8.
THURSDAY, 21st.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "The Art of Working Metals in Japan," by W. Gowland, F.C.S.

Chemical, 8. "The Diphenylbenzenes—I. Metadiphenylbenzene," by F. D. Chattaway, M.A., and R. C. T. Evans. "Derivatives of Camphoric Acid," by Dr. F. S. Kipping. "Some Substances exhibiting Rotatory Power both in the Liquid and Crystalline States," by W. J. Poles.

FRIDAY, 22nd.—Royal Institution, 9. "Hysteria," by Prof. J. A. Ewing, F.R.S.

Physical, 5. "On Dielectrics," by R. Appleyard. "The Field of an Elliptical Current," by J. Viriamu Jones. "An Instrument to Measure Frequency," by A. Campbell.

SATURDAY, 23rd.—Royal Institution, 3. "Three Emotional Composers—III. Liszt," by F. Corder, Curator, Royal Academy of Music.

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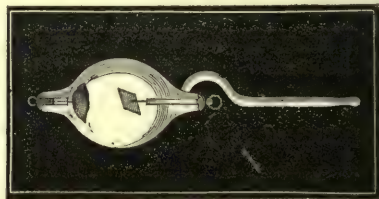
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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1904.

A NEW KIND OF RAYS.

ACCORDING to Röntgen's most recent communications in the *Transactions of the Würzburg Physical Society*, the X rays are able to discharge electrified bodies exposed to the air; the discharge ensuing the more rapidly the more intense the rays. Hereby, it is in general indifferent whether the electric substances are conductors or non-conductors. In an electrified conductor surrounded with a solid insulator, e.g., paraffin, the effect of the irradiation is the same as on stroking this insulating coating with a flame conducted off to the earth. But if the insulating coating is surrounded with a tightly-fitting conductor connected with the earth, and pervious to the X rays, no effect of the X rays can be shown upon the inner electrified substance. The discharge of electrified bodies which are not touched themselves by the X rays can be effected also by air irradiated by the X rays. A brief contact of the air with a body of a large surface is sufficient to annul the property communicated to the air by the X rays. The discharge of electrified bodies by the X rays takes place also in an atmosphere of hydrogen. In tubes highly exhausted, the discharge of a substance which has been directly exposed to the X rays is much slower than in vessels filled with air or hydrogen at the ordinary pressure. In many cases it is advantageous to interpolate between the discharging apparatus furnishing the X rays and the Ruhmkorff spark inductor, a Tesla transformer, as the discharging apparatus is not so readily perforated, and many apparatus yield more intense X rays. As regards the investigation on the origin of the rays, it appears that all solid bodies are capable of yielding X rays under the influence of the cathodic rays; among metals, platinum is the one with which we can obtain the most intense rays. Latterly, Röntgen employs a discharging apparatus in which the cathode is a concave mirror of aluminium, and the anode is a sheet of platinum placed in the centre of the curvature and inclined at an angle of 45° towards the axis of the mirror. In this apparatus the X rays emanate from the anode. The intensity of the rays is perfectly independent of their production from the anode or the cathode. — *Chemiker Zeitung*.

ON THE FUSIBILITY OF PLATINUM IN A CARBON BLAST FURNACE.

By VICTOR MEYER.

IN a memoir from the pen of a thorough expert it has been recently pointed out that the oft-repeated assertion of the fusibility of platinum in a furnace fed with carbon and air has not been incontrovertibly demonstrated. As the vessels used are in general more or less injured at the high temperature of the experiment, or cannot be considered as perfectly fitting, it is not impossible that the flames of the furnace or burning particles of carbon may come in direct contact with the platinum. But, as is well known, in almost every flame there is a hot region having a higher temperature than the melting-point of platinum. A capillary platinum wire can be fused in the hottest part of the flame of a candle. The problem of fusing platinum in the carbon blast furnace in vessels perfectly closed on all sides does not seem to have been hitherto solved in a manner which excludes all doubt.

In the course of the pyro-chemical investigations which for some time have engaged me, in concert with Dr. von Rocklingshausen and Dr. Locke, we have undertaken the task, among other things, of obtaining a fire-box in which platinum can be fused, whilst an alloy of 25 per cent iridium and 75 per cent platinum remains unattacked. We needed such a fire-box for determinations of the density of gases and measurements of temperature, which are undertaken with the apparatus made for us by Hæraeus, of platinum-iridium.

For this purpose we used a furnace quite similar to the blast furnace used by C. Langer and myself, though of larger dimensions, and especially provided with a much larger wind-chest. As fuel we used retort-graphite, broken up in pieces of the size of a hazel-nut. The air was supplied by a very powerful blast. Under certain conditions this furnace answers the purpose required, as is proved by the following experiment:—

We formed a block of perfectly refractory earth in which were two depressions, so that it might be regarded as a double crucible with very thick sides. In one of these depressions was laid a piece of sheet platinum, and in the other a sheet of metal of equal size of the alloy of 25 parts iridium and 75 platinum, which we had previously proved to be considerably less fusible than platinum. The block was then perfectly closed by means of a top of the same refractory earth, so that the whole formed a massive stone-like mass with two cavities.

On burning, the crucible thus formed was converted into a stone perfectly solid and hard. After it had been heated in the above graphite blast furnace, and allowed to cool, it was broken open. The platinum was melted into a ball, but the platinum-iridium alloy was perfectly unaffected.

Hence we must add to the above-quoted remark of H. Hecht the supplement, that now the fusibility of platinum in thick-sided crucibles with a carbon blast furnace is indubitably established. The metal had neither been contaminated with particles of carbon nor by any constituents of the crucible. The platinum-iridium alloy had retained its outer form and its lustre quite unaltered. The admission of furnace gases had been obviated in our experiment much more perfectly than with any previous arrangement of apparatus.

ARGON AND HELIUM IN THE SYSTEM OF THE ELEMENTS.

By W. PREYER.

WHAT places in the system of the elements must be assigned to the indifferent gases argon and helium, as well as to the element discovered by Runge and Paschen in the gases obtained from clèveite (having a lower molecular weight than helium), and not yet named, is a far-reaching question. On the reply, it may depend whether an attempt to represent certain properties of the elements as periodic functions of the atomic weights has a prospect of success. As long as a fixed place in the system has not been allotted to every single known element, all attempts to ascertain the nature of these functions are premature, since we must first establish how many and what elements constitute a period.

Hitherto, in the series from hydrogen to uranium, arranged according to the atomic weights, no single period has met with universal recognition. No one denies that periods exist, but we can no longer—as before the discovery of the two gases with the atomic weights 4 (He) and 20 (Ar)—accept as given the five periods, i.e., lithium—fluorine, sodium—chlorine, potassium—manganese, copper—bromine, silver—iodine, in addition to the fact that iron, nickel, and cobalt, and the platinum metals, as also the metals of the rare earths, in all projects disturbed the assumed and desired symmetry.

In addition, we have the necessity of placing tellurium, not before, but after iodine; since, according to the most trustworthy determinations (both of Brauner and of Standenmair) it has an atomic weight of from 127.6 to

same solution of zinc chloride, in which ordinary silk is at once dissolved on slight heating, does not entirely dissolve tussah silk, even on prolonged boiling. We have further to notice the behaviour of tussah silk on combus-

±	+	+	+	±	-	-	-	±	±	±	+	+	+	±	-	-	-	±
He	Li	Be	Bo	C	N	O	Fl	As	21	22	Na	Mg	Al	Si	P	S	Cl	37
38	Ka	Ca	Sc	Ti	Va	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br	82
83	Rb	Sr	Yt	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	—	I	Te
130	Cs	Ba	La	Ce	Nd	Pr	—	—	Sm	—	—	Gd?	—	Tb	—	Er	—	Dp?
Yb	—	—	—	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—	217
—	—	—	—	Th	—	U	—	—	—	—	—	—	—	—	—	—	—	—
	I.	II.	III.	IV.	III.	II.	I.				I.	II.	III.	IV.	III.	II.	I.	

127.7. Its specific heat points in the same direction. An element, 125, with a rather higher specific heat than tellurium and more strongly electro-negative, has yet to be discovered.

If, now, in order to meet these new requirements, without shaking the established relational affinities of the elements, we for the present regard, in the quest for the natural periods, exclusively their electro-chemical behaviour and their valence, the electro-positive, the electro-negative, and the electrically indifferent elements must be placed together according to their ascending atomic weight. The accompanying table shows the result when hydrogen and the new, not as yet named, gas are placed first.

The slightest and most fluctuating electro-chemical tension is found in the elements of the helium line, of the C and Sr line, and the triple argon-platinum line, and of the triple line to the right in which tellurium has its place.

The Roman characters show the valence of the elements placed above. Where they are absent the valence is still uncertain and may be smaller than 1.

The atomic heat increases in every vertical column from above downwards.

The evidence for these and other systematic relations is found in the author's work ("Das genetische System der Chemischen Elemente," Berlin, Friedlander, 1893). The table is there lithographed. I have here added three elements subsequently discovered, and the new elements thereby postulated, which, like all the $\pm$ elements not belonging to the carbon-silicon stem, lie quite near to the axis of the abscissæ.

In this graphic representation, as shown in the above table, the periodicity appears so distinctly that mathematical speculation might already take up the question of what kind may be the dependence of the properties of the elements (quantitatively determinable) on their atomic weight.—*Berichte*, xxix., p. 1040.

RECOGNITION OF TUSSAH SILK IN TEXTILE GOODS.

By Dr. F. FILSINGER.

TUSSAH silk is distinguished microscopically from true silk (that secreted and spun by the larva of *Bombyx mori*) in that the cocoon thread has a flatter section and a greater breadth; it contains numerous fine air-channels running axially, and numerous intersections, generally placed obliquely. Still more significant is the chemical behaviour of the tussah silk. It is well known that the basic solution of zinc chloride, the alkaline solution of copper glyceride, and concentrated hydrochloric acid, dissolve the silk of *Bombyx mori* easily and completely. On the other hand, tussah silk resists these reagents so persistently that they are slowly and imperfectly dissolved, leaving behind a stratum of sericin which merely swells up, so as to convey the impression of insolubility. The

tion, and the odour given off. If we approximate some twisted-up threads of ordinary silk to a flame, so that it merely touches the ends, they are certainly kindled; but the silk does not go on burning, and forms a globular coalescent mass, giving off the intense and characteristic odour of burning horn and hair. Tussah silk burns much more vividly, probably in consequence of the numerous air-channels; it glows on like cotton, and emits little of the odour of highly nitrogenous substances. Of course for these tests the specimen must be prepared by treatment with dilute hydrochloric acid, and careful washing to remove dye and dressing. As I had not at my disposal any references on the percentage of nitrogen in the various kinds of silk, it was determined in my laboratory by the Kjeldahl process, with the following results:—

	Silk of <i>B. mori</i> .	Tussah silk.
Moisture (105°)	8.85	9.10
Nitrogen (a)	16.09	14.34
„ (b)	16.45	14.45

But although the nitrogen of ordinary silk is thus greater in proportion than that of the tussah silk, the difference is scarcely enough to explain the difference of the odours on combustion.

Under these circumstances chemical tests must, for the present, be laid aside in the detection of tussah silk, and our reliance must be placed on microscopic examination.—*Chemiker Zeitung*.

DETERMINATION OF ANILINE IN PRESENCE OF SMALL QUANTITIES OF TOLUIDINE, AND THE DETERMINATION OF TOLUIDINE IN PRESENCE OF SMALL QUANTITIES OF ANILINE.*

By P. DOBRINER and W. STRANZ.

SOME time ago H. Reinhardt (*Chemiker Zeitung*) gave a method for the determination of aniline in its mixtures with toluidines. A basis was thus given for the examination and valuation of those very important products, the aniline oils.

The method depends on the fact that the action of nascent bromine converts aniline into a ter-bromine derivative and the toluidines into dibrom derivatives.

The bromine liquid is standardised with pure aniline, and the standard for toluidines is then found by multiplication with—

$$\frac{160.5}{93} \text{ (see below).}$$

If the aniline oil contains only a mixture of aniline and the two toluidines and is perfectly anhydrous, a direct

* A communication from the analytical laboratory of the Colour-Works formerly F. Bayer and Co.

titration gives both the proportion of aniline and that of both the toluidines.

The calculation of the proportion of aniline appears, from the equation,—

$x = 2.3777 vt - 1.3777 a$, in which a = the quantity of aniline oil used.

x = the quantity of aniline present.

t = the standard of the bromine liquor for pure aniline.

v = the number of the c.c. of bromine liquor consumed.

$a - x$ is then the quantity of the toluidines present in the aniline oil.

We have undertaken to test the applicability of this method if one of the components is present only in a small quantity.

The examination and valuation of the aniline oil for blues, of ortho- and para-toluidine, has been effected hitherto by the determination of the physical constants,—boiling-, fusion-, and congelation-points, specific gravity, solubility, &c. All these investigations admit of a conclusion as to the purity of the specimens in question only if executed with the most anxious care. An accurate determination of the impurities present is not thus rendered possible, and it was therefore of interest to ascertain if Reinhardt's method is sufficiently accurate for the purposes above mentioned.

As appears from the analyses quoted, the method admits of the detection and determination of small quantities of toluidine in aniline. The formula above given can be used in calculating the results.

On the contrary, the methods prescribed by Reinhardt for the titration of aniline alone, or in its admixtures with small quantities of aniline, give results not perfectly accurate. On applying the aniline standard we find in pure toluidine the presence of aniline, and in mixtures of toluidine with small quantities of aniline the proportion of the latter comes out too high. If we use, in titrating pure toluidine, the standard for toluidine calculated from the aniline standard, we obtain a result too high by about 1 per cent. The cause of this phenomenon is perhaps, on the one hand, that the error made in calculating the toluidine standard from that of aniline is double, and, on the other, that in the toluidines the substitution is less smooth than in the titration of aniline.

In paratoluidine the substitution ensues at first slowly, and we therefore, to avoid loss of bromine, add the bromine lye less rapidly. When the reaction is at once initiated, the titration proceeds here smoothly to completion.

In the titration of both toluidines a yellow colouration of the substitution products is observed, due probably to a slight oxidation.

It is also not impossible that in this kind of bromation there are formed small quantities of a mono-substitution product, which tell in the titration of pure toluidine or in presence of small quantities of aniline. If both constituents are present in about equal quantities in aniline oils, or if the aniline predominate, an error occasioned by the formation of a mono-substitution product would not come into consideration. We are still engaged with ascertaining the exact cause of the phenomenon above mentioned.

We have now found that Reinhardt's formula is sufficiently applicable in the examination of toluidine or its mixtures with small quantities of aniline, if we complete the standardising of the bromine lye for pure toluidine, and inversely calculate the standard for aniline by multiplication with—

$$\frac{93}{160.5}$$

In general it may be recommended to standardise both or pure aniline or pure toluidine. Let t and T be the

corresponding standards. The proportion of aniline x will then follow from the equation—

$$\frac{x}{t} + \frac{x - a}{T} = v.$$

As a matter of course Reinhardt's method permits of the examination of the salts of aniline and the toluidines. The determination must be effected also in the anhydrous substances dried over sulphurous acid. The examination of aniline hydrochlorate, the aniline salt of commerce, is especially important.

Reinhardt's formula then passes into the following:—

$$X = 2.5102 V T - 1.5102 A.$$

Here signify—

A = the quantity of aniline salt taken.

X = the proportion of aniline hydrochlorate therein contained.

T = the standard of bromine lye for pure aniline hydrochlorate, which may also be obtained from the aniline standard t on multiplication by—

$$\frac{129.5}{93}$$

V = the number of the c.c. of bromine lye consumed.

—*Zeit. Anal. Chemie.*

CHEMICAL VERSUS BACTERIOLOGICAL EXAMINATION OF POTABLE WATER.

By W. P. MASON.

APROPOS of the recent articles upon this question, which have appeared in the English papers, it is noteworthy that there is a growing tendency among physicians and civil engineers to belittle the chemist's opinion regarding the potability of a water, and to pin their faith exclusively upon what the bacteriologist may have to say upon the subject. This feeling is strengthened by the publication of the results of such trials as that undertaken by the London Local Government Board, in which, it will be remembered, water samples purposely inoculated with typhoid germs were sent for analysis to one of England's leading chemists, and were by him pronounced pure.

Those who set special value upon such a "test" of methods as the above, and who consider it quite final as showing the inability of chemistry to detect pollution in a liquid which the bacteriologist would instantly pronounce very foul, should remember that such a sample of water could not be found in practice, and that the very conditions under which it was prepared eliminated the chemical items indicating pollution, while it increased tremendously the signs governing the bacteriological side of the case.

The bacteriologist sought for the Eberth bacillus, and, very naturally, quickly found it in a water purposely sown with a culture of the germ.

The chemist looked for those elements which always occur in sewage-laden water, whether the sewage be from sources of disease or otherwise, and, not finding them, he pronounced the water to be what it really was, free from sewage addition.

Sewage, as it occurs in practice, contains an immense deal of material other than that productive of disease, and it is upon just this comparatively harmless, but constantly present material, that the chemist relies for the indication upon which he bases his opinions.

He is unable to say whether or not a sewage-laden water is disease-bearing on any particular date, for to him all sewage is alike; but he condemns the water, for the reason that, although it may be harmless to-day, it is impossible to predict what may be its condition to-morrow.

Within the week I have been requested to make a

bacteriological examination of the water of a certain well, in order to determine if it be affected by neighbouring cesspools.

The physician who made the request was impressed with belief in the paramount value of such an examination and the comparative uselessness of chemical analysis.

I am quite convinced that, had I followed his suggestion, I should have sought in vain for any specific microbe; but inasmuch as upon chemical analysis I found that the "chlorine" ran twenty-four parts per million, which is about ten times the local "normal," and the "nitric nitrogen" read nine parts per million in place of 0.116, I condemned the water off hand without going further.

There is simply no comparison between the two methods in question for water problems of this class, and the value of chemistry is still more pronounced in those instances where it is possible to introduce common salt or lithium chloride into a source of suspected pollution, and then look for increased chlorine or presence of lithium in the water of the well. In legal cases touching upon this point of contamination of wells, by cemeteries for instance, the chemical testimony is especially strong.

In the matter of determining the suitability of a stream for city supply, the services of the bacteriologist should be unquestionably secured, but it is doubtful if his report can be considered of more importance than that of the chemist.

Chemical analysis, by comparing the water taken at the site of the proposed intake with that from the same stream above all points of possible pollution, can indicate whether or not up-stream contamination is felt at the lower point; nor is it necessary that the polluting sewage be from pathogenic sources in order that its presence may be recognised.

As Dr. Dupré has pointed out, chemistry in such cases anticipates what may happen in the future, and, by timely advice, may prevent an outbreak of disease, while, on the other hand, the discovery of disease germs in a water is only possible after the water has become infected.

Bacteriology is of especial value, and greatly superior to chemistry for the testing of filters and watching any variation in their efficiency.

For this purpose the simple count of germs per c.c. is most valuable, and differentiation is a secondary matter; for the assumption is a just one, that a filter which will remove the harmless bacteria will take out the objectionable ones as well.

It is very far from my desire to decry the value of bacteriology; but I cannot but feel that, in their enthusiasm over the great triumphs of the new science, the people at large have gone slightly "bacteria mad," and are apt to expect more than can be furnished by the means and information now available.—*Journal of the American Chemical Society*, vol. xviii., No. 2, Feb., 1896.

A REVISION OF THE ATOMIC WEIGHT OF ZINC.*

FIRST PAPER: THE ANALYSIS OF ZINCIC BROMIDE.

By THEODORE WILLIAM RICHARDS

and
ELLIOT FOLGER ROGERS.

(Continued from p. 227).

Balances and Weights.

THE preliminary determinations were made upon a long-armed Becker balance with the help of very carefully standardised platinised brass weights. The final deter-

minations were made upon the admirable Troemer balance procured for the research upon copper, and subsequently used for those upon barium and strontium. The weights used in these final determinations were the same as those used in the researches just cited; they were compared with one another at the beginning and at the close of the research, with satisfactory results. All weighings were made by substitution, the tare weights being vessels as nearly as possible similar to those being weighed; and all were reduced to the vacuum standard by the usual formula.

The Specific Gravity of Zincic Bromide.

In the course of recent investigations upon the atomic weights, so many of the usually accepted specific gravities of hygroscopic substances have been found to be seriously in error, that it seemed advisable to re-determine the constant which influences the reduction to vacuum of the present results.

Pure zincic bromide was dried for a long time at a temperature of 200°, and then fused and heated for a short time at 300°. The pycnometer, in which this drying was effected, was then stoppered and cooled in a desiccator. Carefully dried toluol, having a specific gravity of 0.8646 at 20°, when referred to water at 4°, was used as the liquid to be displaced. Toluol is convenient for the purpose, because so few inorganic substances are soluble in it, and because its volatility is not so great as to cause serious loss during the weighing, but is great enough to allow of the rapid drying of the exterior of the apparatus. The first sample of zincic bromide was made from very pure hydrobromic acid and ordinary pure zinc, and was distilled in an atmosphere of carbon dioxide; the second was made from the purest electrolytic zinc and the purest bromine. Both samples gave a perfectly clear dilute solution in water after the expulsion of the toluol on the steam-bath after the experiment. The decanted toluol left upon evaporation on the steam-bath only a trace of residue, which was insoluble in water. Water decanted from this residue gave no trace of precipitation with argentic nitrate; hence it is evident that zincic bromide is insoluble in toluol. The liquid contained in glass increases about 0.001 of its apparent volume for each degree of temperature; and the small appropriate correction is applied below.

Specific Gravity of Zincic Bromide.

No. of expt.	Weight of ZnBr ₂ Grms.	Temperature. Degrees.	Weight of toluol displaced. Grms.	Water at 40° corresponding to toluol. Grms.	Sp. gr. at 20°.
1.	3.8856	19.8	0.7960	0.9206	4.220
2.	11.2394	20.3	2.303	2.664	4.218

Average.. .. 4.219

The value 4.22 is used in the work which follows. In this connection it may be of interest to compare the specific gravities of the substances recently determined here.

Specific Gravities compared with Water at 4°.

Substance.	Old values.	Former experiments.	New values.	Temperature.
Anhydrous BaCl ₂	3.85	{ Quinke Favre & Volson Schroeder	3.86	24°
BaBr ₂	4.23	Schiff	4.79	24°
SrBr ₂	3.96	Bödeker	4.22	24°
ZnBr ₂	3.64	Bödeker	4.22	20°
Crystallised BaCl ₂ ·2H ₂ O	3.05±	{ Joule & Playfair Schiff Schroeder	3.10	24°

Preliminary Analyses of Zincic Bromide.

Preparation of Zincic Oxide.—The zincic bromide used for the first series of experiments was made by the action of pure hydrobromic acid upon pure zincic oxide.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*. Presented April 10, 1895.

For the preparation of the oxide, "pure" zinc of commerce was dissolved in pure dilute sulphuric acid, and the solution was allowed to remain over an excess of the metal for several weeks. The filtered solution was acidified with sulphuric acid, warmed, and treated with well-washed hydric sulphide, until a considerable mass of pure white precipitate had formed.

observed that the sodic carbonate occluded in the quantitative precipitation of zinc may be easily removed in this way, and the present experience showed that occluded zinc chloride could be washed away with equal ease. The zinc oxide thus obtained was almost white, with a very faint tinge of yellow; upon solution in nitric acid it gave absolutely no opalescence with argentic nitrate. Its

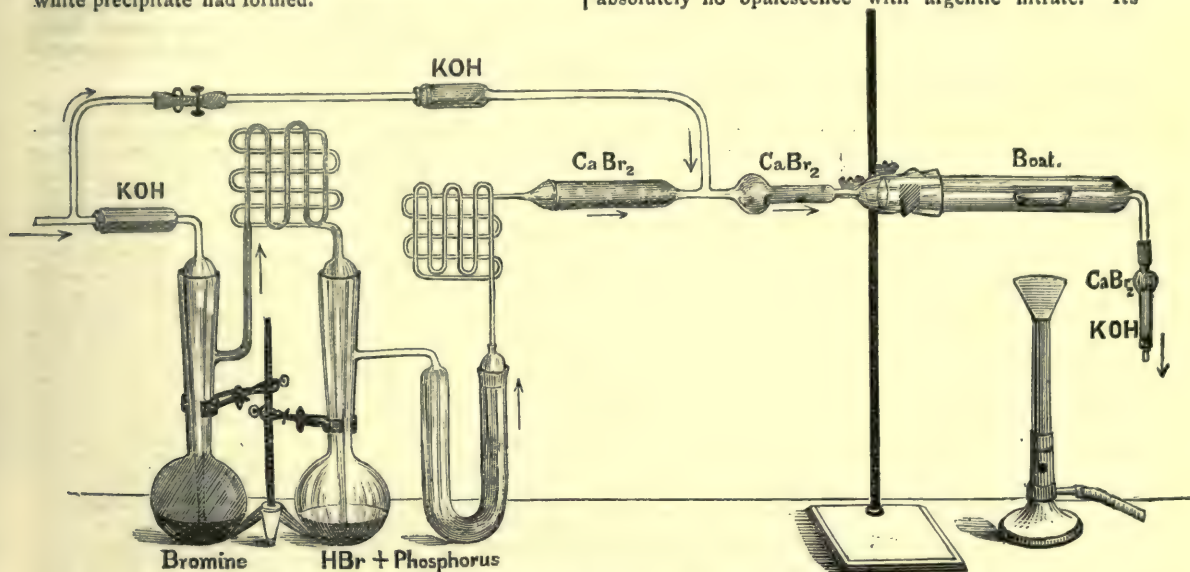


FIG. 1.—APPARATUS FOR FUSING ZINCIC BROMIDE.

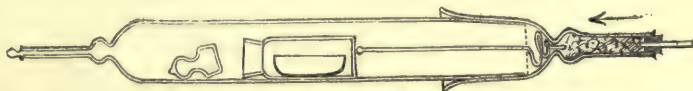


FIG. 2.

(Pure dry nitrogen and argon enter the apparatus (Fig. 1) through the tube at the left. The arrangement for preparing this mixture is not shown. Upon closing the pinchcock in the upper left-hand corner the gases are driven through the flasks and charged with dry hydrobromic acid; upon opening the pinchcock, the hydrostatic pressure causes the gases to flow through the upper short cut tube and effectually to sweep out the acid from the fusion tube. This latter tube, containing the boat in which the zincic bromide is fused, is at the right of the figure).

The strongly smelling filtrate from this zincic sulphide, now freed from all traces of the most usual metallic impurities, was treated with chlorine water to oxidise any iron or manganese which might be present, and precipitated fractionally with pure sodic carbonate. The first fraction of the precipitate containing traces of iron and manganese was thrown away.

After a thorough washing, the second fraction, containing most of the zinc, was dissolved in pure nitric acid, keeping the carbonate in excess. After filtration, the addition of a little ammoniac carbonate, and another filtration, the greater part of the zinc present was precipitated by means of ammoniac carbonate. When it had been subjected to a thorough washing, the basic zinc carbonate was ignited in a double platinum crucible over an alcohol lamp. The oxide thus obtained was washed repeatedly with water; for often an impurity which is held by a wet precipitate may be washed out when the precipitate has been partially decomposed or disintegrated by heat. Artus (Berzelius, *Jahresberichte*, xxiii., 132) has

method of preparation made the presence of non-volatile impurities almost impossible, for it was precipitated from a solution containing nothing but zinc, nitric acid, and ammonia.

Preparation of Hydrobromic Acid.—This substance was made by the action of bromine on water in the presence of phosphorus. The bromine was purified by the well-known method of Stas (*Mém. Acad. Belg.*, xliii., Pt. 2, 90, 38), having been dissolved in a saturated solution of potassic bromide holding zinc oxide in suspension, and distilled from this solution after long standing. The bromine, thus freed from chlorine and iodine, was collected under water and re-distilled. Red phosphorus was now purified by very fine pulverisation under water and by repeated washing of the powder with pure water. According to Stas, this method removes every trace of chlorine which may be held by the substance. Our own experience has not been uniformly favourable in this respect, but upon this occasion and several others both the qualitative tests for the absence of chlorine and the quantitative analysis of the hydrobromic acid made with the assistance of well washed phosphorus were satisfactory. The bromine was allowed to act upon the phosphorus and water with the usual precautions in an apparatus made wholly of glass. The acid thus formed was distilled in five fractions, of which the first consisted chiefly of water and a trace of bromoform. Only the last fraction of the distillate containing perhaps a third of the bromine taken, was used in the work; and this was re-distilled with the further rejection of the first and last portions. The remainder was analysed quantitatively

with pure silver in order to test its freedom from chlorine, with very satisfactory results. The silver was prepared, weighed, and dissolved with great care, the precipitate was collected upon a Gooch crucible, and all weighings were reduced to the vacuum standard.

Purity of Hydrobromic Acid.

No of experiment.	Weight of silver.	Weight of argentic bromide.	Per cent of silver in argentic bromide.
3.	1.86058	3.23884	57.446
4.	1.72320	2.99983	57.443
Average.. ..			57.444
Stas found			57.445

Preparation of Zincic Bromide.—For Experiments 5 and 6 zincic bromide was made by simply dissolving in a platinum dish the pure oxide in the pure acid described above. For Experiment 7 similar zincic bromide was sublimed in a wide glass tube in a current of pure dry carbon dioxide. The next experiment, No. 9, was made with similar zincic bromide prepared wholly in glass and not sublimed. A large portion of the substance was then prepared by exact neutralisation and evaporation in a platinum dish, a strip of pure zinc was added to precipitate a trace of platinum—which had been dissolved because of the presence of traces of oxidised nitrogen in the oxide—and the whole was subjected to crystallisation. The mother-liquor served for Analysis 8, and the pure white crystals for the third series of preliminary determinations (Experiments 10, 11, 12, and 13).

Preparation of Silver.—This substance was prepared by the method described in a recent paper on the atomic weight of barium (*Proc. Amer. Acad.*, xxviii., 22; xxix., 64).

Pure argentic chloride was reduced by means of pure sodic hydrate and invert sugar, and the metal was washed and fused in a gas flame upon charcoal. The lumps thus obtained were dissolved in pure nitric acid and precipitated by electrolysis. The beautiful crystals of electrolytic silver were rapidly fused upon cupels of sugar charcoal (*Proc. Amer. Acad.*, xxix., 65) in the flame of illuminating gas, and cooled in a reducing atmosphere. Such silver is essentially identical with the much more carefully prepared metal used in the final experiments, and gives every evidence of being pure within two or three parts in a hundred thousand (*Proc. Amer. Acad.*, xxix., 65). A solution of argentic nitrate through which over 50 grms. of such silver had passed by electrolysis, was found upon suitable treatment to yield only half a m.grm. of baric sulphate; hence the silver could not have contained more than two parts of sulphur in a million.

Preparation of other Materials.—Nitric acid was repeatedly distilled, the last portion of the distillates being used. It is needless to say that it was wholly free from halogens. The sulphuric acid used for analytical purposes was distilled with great care; that used for desiccators was boiled with a little ammoniac sulphate. The water used in the preliminary determinations was twice distilled in a tin condenser. In order to avoid the introduction of chlorine, carbon dioxide was prepared at first from acid sodic carbonate and sulphuric acid, later from dilute nitric acid and marble. Nitrogen mixed with argon was prepared by passing a mixture of air and ammonia over red-hot copper. Both gases were very thoroughly washed.

Methods of Analysis.—The necessity of driving out every trace of water from the substance to be analysed was the precaution upon which most labour was expended. The low boiling-points of zincic bromide makes it possible to distil the substance easily in a hard glass tube. Accordingly, for the first series of very crude experiments pure zincic bromide was distilled in a tube provided with bulbs, which were sealed off when filled. In order to obviate the introduction of an error from the additional weight of the atmosphere of carbon dioxide in which the

distillation took place, the bulbs were heated to about 120° at the moment of sealing. The bulbs were weighed after scratching them upon each end with a file; and after the zinc bromide had been dissolved out the glass was weighed alone. The bromine present was weighed as argentic bromide, and the atomic weight of zincic was calculated from the ratio of argentic and zincic bromides. The more trustworthy results ranged from 65.40 to 65.54, with an average of 65.47; but it was clear that the method admitted of too many possibilities of error to yield satisfactory results.

Hence the method which answered well in the recent analysis of strontic bromide (*Proc. Amer. Acad.*, xxx., 369) was adopted here. The pure re-crystallised or sublimed zincic bromide was placed in a platinum boat and kept for some time in an atmosphere of pure dry nitrogen charged with pure hydrobromic acid. It was found that in this way all the water could be expelled from the salt without the introduction of a trace of oxybromide; indeed, zincic bromide which by rapid heating in the air had been partly decomposed could be speedily brought back to its normal condition by fusion in the atmosphere of dry dilute hydric bromide. The presence of the insoluble oxybromide is easily detected by dissolving the bromide in large amounts of water; in every case the bromide used in the analyses below gave an absolutely clear solution. Baric and strontic bromides ignited in the same way give solutions which are absolutely neutral to methyl-orange and phenolphthalein; hence it is most likely that the zincic bromide, which does not admit of similar alkalimetric testing, is also quite normal. For the details the paper upon strontium must be consulted, but a sketch of the apparatus will probably suffice (Fig. 1). In the present case hydrogen could not be added to the nitrogen for fear of reducing some of the zincic bromide; but no trouble was experienced from corrosion of the boat. When the substance had been kept for some time in a state of tranquil fusion, and had just solidified, the boat was quickly slid into a weighing tube, which was in its turn placed in the automatic desiccator tube (Fig. 2). After the tube and boat had been heated to about 200° for some time in a current of pure dry air, the desiccator tube was raised to a vertical position, the stopper being thus allowed to fall into place.

After weighing, the pure zinc bromide was dissolved in water and precipitated by means of a slight excess of very carefully weighed pure silver in very dilute solution. The argentic bromide was collected upon a Gooch crucible, the shreds of asbestos carried through (0.05 to 0.20 m.grm.) were collected upon a very small fine filter, and the total weight of the argentic bromide thus obtained gave one ratio upon which to base the atomic weight of zinc. In the third series the filtrate was all evaporated to very small bulk, and the excess of silver precipitated by hydrobromic acid and weighed upon a Gooch crucible in the same way as the other portion of argentic bromide. By subtracting this excess from the total silver originally weighed out, the weight of silver equivalent to the zincic bromide could be easily found. Great care was taken to exclude daylight, and to carry out all the precautions necessary in accurate work. The data are given below:—

SECOND SERIES.

The Ratio of Zincic Bromide to Argentic Bromide.

No. of analysis.	Weight of zincic bromide. Grms.	Weight of argentic bromide. Grms.	Atomic weight of zinc.
5.	1.69616	2.82805	65.469
6.	1.98198	3.30450	65.470
7.	1.70920	2.84949	65.487
8.	2.35079	3.91941	65.470
9.	2.66078	4.43751	65.400
Average.. ..			65.459

THIRD SERIES.

The Ratio of Zinc Bromide to Silver and Argentic Bromide.

No. of anal.	Weight of zinc bromide. Grms.	Weight of silver bromide. Grms.	Weight of argentic bromide. Grms.	Atomic weight of zinc from Ag_2ZnBr_2 .	Atomic weight of zinc from $2\text{AgBr}:\text{ZnBr}_2$.
10.	2'33882	2'24063	3'90067	65'409	65'400
11.	1'97142	1'88837	3'28742	65'444	65'434
12.	2'14985	2'05971	3'58539	65'396	65'402
13.	2'00966	1'92476	3'35074	65'472	65'463
Average..				65'430	65'425

The second series of results, excepting the last determination, is undoubtedly affected by the presence of water in the zinc bromide; for the methods of drying and transference had not been perfected. The third series was much more carefully made, but even here there was a possibility of the retention of a small amount of water in some of the analyses; hence this result also is probably somewhat too high.

The results of the four analyses of the third series give the following figures for the per cent of silver in the bromide:—57'443, 57'443, 57'447, and 57'443. The mean of these results is 57'444; Stas having found 57'445. It will be remembered that the hydrobromic acid from which the zinc bromide was made gave precisely similar results. This identity proves that the analytical work was without fault, and that argentic bromide does not possess the slightest tendency to occlude zinc bromide when precipitated from dilute solutions. The analysis of the hydrobromic acid proved that the material was free from chlorine and iodine.

Accordingly the rather large variations in the results must be due wholly to the original condition of the samples of zinc bromide. It remained, therefore, to make a final series of determinations upon zinc bromide from which water should have been absolutely excluded; and since one of us was unfortunately called away, this series was made by the other alone.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, May 11th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 167 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 167 samples examined all were found to be clear bright, and well filtered.

The amount of rain which has fallen during the past month is again very much below the average of the last 30 years. The actual rainfall was 0'58 inch, the 30 years' average being 1'66 inches, leaving a deficiency of 1'08 inches, most of the fall occurring between the 10th and 17th of the month. We may add that the total deficiency for the first four months of this year is 3'06 inches.

Our bacteriological examinations gave the following results:—

	Colonies per c.c.
Thames water, unfiltered	1833
Thames water, from the clear water wells of the five Thames-derived supplies..	highest 60
Ditto ditto lowest	16
Ditto ditto .. (12 samples) mean	33
New River water, unfiltered	1501
New River water, from the Company's clear water well	17
River Lea water, unfiltered	1643
River Lea water from the East London Company's clear water well	34

By comparing the above figures with those of the last few months, it will be seen that the quality of the London waters is of great excellence, and that the filtering plant of the several Companies is maintained in a state of high efficiency.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 225).

The Spectrum of Trioxide of Thallium prepared from Lamy's Sulphate.—I repeated several times on trioxide the observations I had made on the metal reduced at the same time. When a platinum wire loop is plunged into well-washed trioxide of thallium, that had been quickly dried and fused in a platinum dish recently heated to whiteness to drive off the sodium derived from the air, and when the loop coated with trioxide is inserted into a hydrogen flame or Bunsen burner, or into incandescent hydrogen, the same phenomena are observed at similar intensities. Spectrum analysis shows the single green line, whether the observation be made with a very narrow slit, or with it wide enough to show a faint or strong continuous spectrum.

Thus, without doubt, the metal and its trioxide, prepared at the same time by electrolysis purified ammoniated sulphate, show the same spectrum as the sulphate itself, which consists of the single green line.

I converted the greater part of the metal and the trioxide produced by electrolysis into sulphate. Having found that the spectra of the sulphates thus produced were identical, I subjected an ammoniated solution of them separately to electrolysis. The metal and trioxide derived from each of them still showed identical spectra, characterised by the single green line. Finally, from the new metal and trioxide, I re-formed sulphates. Thallium and trioxide from the *third regeneration*, when introduced in succession into a hydrogen flame, a dark coal-gas flame, incandescent hydrogen, and finally into an oxy-hydrogen blowpipe at the highest possible temperature, showed, on spectrum analysis, either a dark or luminous spectrum, both marked with a *single and isolated green line*, incapable of being split up.

Such, in fact, is the spectrum of the metal in the sulphate of thallium prepared by the late M. Lamy.

The Flame Spectrum of Chloride of Thallium.—I converted the greater part of the metal and trioxide into sulphates, and these sulphates into chloride of thallium; after washing, it was dissolved twice in boiling water, and the solution precipitated by means of hydrochloric acid. When properly separated from the mother-liquor, by means of a wash-bottle, and introduced, on a platinum wire loop overlaid with iridium, into a pure hydrogen flame, a Bunsen flame, and into incandescent hydrogen, it showed, on analysis of these flames, a spectrum characterised by a single green line, on a dark or bright background, according to the width of the slit. The platinum wire loop was not attacked by chloride of thallium; the thallic spectrum disappeared when the chloride was volatilised,—a phenomenon which did not occur with the metal and trioxide, for they attacked and penetrated the platinum.

I shall refer later on to the position of the line shown by chloride of thallium, already fixed by M. Bunsen.

When left under a bell-jar to dry, it occluded sodium, but so slowly that it only showed the sodium line after four or five days exposure, when sheltered from air dust.

The Flame Spectrum of Carbonate of Thallium prepared by Mr. Crookes.—After having separated the small quantities of barium and calcium contained in the carbonate of thallium sent me by Mr. Crookes, this salt, when introduced into a hydrogen or oxyhydrogen flame, showed, on spectrum analysis, a spectrum consisting of the thallium and sodium lines. No other line was visible. In the last chapter I described the reason why I could not get rid of the latter line. Later on I shall return to the spectrum of pure carbonate of thallium.

The Flame Spectrum of Mr. Crookes's Thallium, and of the Metal obtained by purifying Commercial Thallium.—I described at some length, in the last chapter, the method I adopted for purifying the thallium sent me by Mr. Crookes. I applied the same method for preparing thallium from my commercial metal.

The final result having been the same, I can limit myself to saying that the metal obtained by electrolysis an ammoniated sulphate showed the same spectrum as the metal I prepared by electrolysis the ammoniated sulphate purified by the late M. Lamy. When varying the method of volatilising the metal, and working on seven different samples, the spectrum, dark or bright according to the width of the slit, always consisted of the same single green line. The flame spectrum of thallium is therefore absolutely the same as that originally described by Messrs. Crookes, Lamy, Bunsen, and Kirchhoff.

I will say the same with regard to the spectrum of the trioxide produced at the same time as the metal, by electrolysis the ammoniated sulphate. The vapour of this trioxide, obtained at a temperature near the fusing-point of iridium, only showed, on spectrum analysis, the single green line, on a dark or bright background, according to the width of the slit and the part of the vapour examined.

This conclusion was confirmed by the observations I made on the flame spectra of chloride, bromide, and iodide, obtained from the sulphate used to produce the thallium and its trioxide. In fact, the spectra of the three thallium compounds are identical with those of the metal derived from the sulphate, and of Lamy's sulphate, chloride, and metal.

My researches on bromide and iodide enable me to say that these compounds do not impart to a hydrogen flame that brilliant pure green tint seen with the metal, trioxide, sulphate, and chloride. With an equal amount of metal introduced into the flame, its tint is much paler and duller, and approaching to blue. It appears to me that at the temperature of burning hydrogen and coal-gas in air, and much more so at the temperature of hydrogen made incandescent by burning in oxygen, bromide and iodide are dissociated, that the bromine and iodine are set

free, and thus help to change the colour characteristic of a thallium flame.

Whatever may be the cause of it, the thallium spectrum remains the same as regards the singleness of the line.

On the Flame Spectrum of Thallous Hydrate, Carbonate, and Nitrate, obtained directly from Pure Metal.—I wished to carry my investigations as far as possible. For this purpose I converted into thallous hydrate, carbonate, and nitrate, part of the metal crystallised in large flakes, obtained by electrolysis pure sulphate. In the last chapter I described the means I used for this end.

I also had occasion to note the identity of the spectra of thallous hydrate, carbonate, and nitrate with that of the metal from which they were derived. I found, at the same time, that at the instant they were produced, hydrate and carbonate contained sodium, probably occluded from the air used to oxidise the metal, whilst the solution of nitrate did not show the sodium line immediately after the metal was dissolved in pure nitric acid; but, when left to itself to evaporate, crystallised nitrate showed the sodium line as plainly as crystallised carbonate, and that it was sufficient to re-dissolve them and precipitate the solution by means of absolute alcohol, in order to so far free them from sodium that they no longer showed the sodium spectrum with that of thallium.

From the above work I conclude that the flame spectrum of thallium, and such of its compounds as can be obtained sufficiently pure, consists simply of the single line to which we owe the discovery of the metal.

On the Electric Spectrum of Thallium and its Principal Compounds.—I commenced this research by examining the electric spectra of thallous sulphate and chloride, obtained from Lamy's sulphate. An induction spark was passed, from a coil with a condenser, capable of giving sparks 5 c.m. in length, between platinum balls from 2 to 3 m.m. apart, and coated with sulphate or chloride, fused or moistened. When using them fused, the spark was barely coloured green; on the other hand, it was a very intense pure green when the sulphate and chloride were moistened with a saturated solution of the same. On spectrum analysis of a thallic spark, passing either vertically or horizontally, and using a sufficiently narrow slit, the spectrum consisted of a single line on a dark background, the line being pure green and not very brilliant with fused sulphate and chloride, and pure green and very intense when these compounds were kept moistened.

Under the given conditions,—that is to say, with purified chloride and sulphate, and electrical phenomena of the above-mentioned intensity,—the sodium and air lines were entirely absent.

In order to ascertain the actual cause of the absence of the sodium and air lines, I substituted for the platinum balls coated with sulphate or chloride, clean platinum balls, also fixed from 2 to 3 m.m. apart. After passing a series of sparks, and noting the appearance of the sodium and principal air lines, without breaking the current, I coated the balls successively with a thin paste of pure sulphate and chloride. At the very moment the sparks became green, the spectrum, which was more or less luminous, owing to the air lines, became dark, the air lines and the sodium line disappeared, and were replaced by a single strong pure green line. The thallic rays from the spark masked the sodium and air lines. This property of masking is real, though very limited.

On coating the platinum balls with moistened thallous sulphate, on which a sufficient quantity of sodium had condensed, by exposure to air under a bell-jar, to show the sodium line persistently in a flame spectrum of thallium, the electric thallium spectrum showed the sodium line, although very faintly. Air lines did or did not appear, according to the relative intensity of the electrical phenomena.

The spark dissociated the thallous sulphate and chloride; it was found, in fact, that after its passage these compounds were very much blackened and coated with peroxide of thallium.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, May 8th, 1896.

Captain W. DE W. ABNEY, President, in the Chair.

MESSRS. FRITH and ROGERS read a paper on "*The True Resistance of the Electric Arc.*"

It was pointed out by Prof. Ayrton at the British Association meeting, at Ipswich, that if the "true resistance" of an arc is defined as the ratio of a small increase of the P.D. between the carbons to the corresponding change in the current, then it follows that this "true resistance" must be a negative quantity.

In order to measure the "true resistance" without appreciably altering the form of the carbons, &c., the authors superpose a small alternating current on the main continuous current. The arc lamp employed was adjusted by hand, and the arc length was measured by projecting an image of the arc by means of a lens. The main (continuous) current and P.D. were measured by a Weston ammeter and voltmeter, while the auxiliary alternating current was measured by means of an air transformer and an electrostatic voltmeter.

The authors find that between the limits employed, the magnitude of the alternating current did not influence the results obtained for the resistance of the arc.

The frequency, so long as it lies between the limits 250—7 complete alternations per second, and the waveform do not influence the resistance, since the same results were obtained with a Pyke and Harris alternator, a Ferranti alternator, a Gramme alternator, and a Mordey transformer.

For each make of carbon examined, four combinations were used: + cored, — cored; + cored, — solid; — cored; + solid, — solid. The general character of the curves obtained is that for the + solid, — solid combination, the "true resistance" is always negative; while for + cored, — cored, it is always positive. The other curves lying between these two extremes; those which have the + carbon solid always being more negative than those which have the + carbon cored.

In the case of the curves showing, for solid carbons, the relation between the resistance of the arc and the P.D. between the carbons, the current being constant (10 amperes), a minimum (maximum negative) value for the resistance occurs at about 55 volts. With combinations having a cored positive this minimum becomes more strongly marked, and occurs at a lower voltage. The authors find that for cored carbons the position of this minimum is closely connected with the presence or absence of the dark space in the arc. For points on the curve to the right of the minimum point, the dark space is absent; while for points to the left of the minimum, the dark space is always present.

It was found that the effect of using as the + carbon a Carré carbon in which the core had been bored out, was to obtain a curve closely resembling that obtained when both carbons were solid. On filling this hollow carbon with plaster-of-Paris or kaolin the resistance of the arc became positive.

The above experiments were made with the + carbon uppermost; other experiments made with the arc inverted showed that with solid carbons the resistance is not appreciably altered by inverting the arc. With cored carbons, however, the resistance, as well as the physical character, of the arc is altered; for, on inversion, the dark space disappears and the resistance considerably diminishes. If, however, the conditions under which the arc is burning are such that the dark space is absent, then inverting the arc does not alter the resistance.

Attempts were made to measure the "true resistance" of a direct current hissing arc, but it was found that even

with the alternator at rest there was a large deflection of the electrometer, showing that the current through a hissing arc was oscillatory.

In order to elucidate the marked difference between their results for cored carbons and those deduced from Mrs. Ayrton's curves, the authors have made a series of measurements at low frequencies. They find that there is a critical frequency above which the resistance has a positive value which is independent of the frequency, and below which it has a negative value: this critical frequency being between 7.5 and 0. In order to investigate the sign of the resistance at low frequencies, the vibrations of the needles of the ammeter and voltmeter were made use of. By an arrangement of mirrors, the needles and scales of both instruments could be observed simultaneously. In this way it could be seen whether the two needles were, at any instant, vibrating in the same or in opposite directions. If the needles vibrate in the same phase, *i.e.*, if an increase of P.D. is accompanied by an increase of current, then the resistance must be positive; while if they are vibrating out of phase, *i.e.*, if an increase of P.D. is accompanied by a decrease in current, then the resistance is negative.

An attempt to run the arc off a continuous current dynamo failed, since, even with the alternator at rest, the electrometer showed a large deflection, evidently due to the oscillation of the current, owing to the commutator of the dynamo bearing a finite number of segments.

Prof. A. GRAY doubted whether it was right to give the name "true resistance" of the arc to the slope of the curve connecting the potential difference (V) and the current (A). The authors' method of deducing $\frac{\delta V}{\delta A}$ was only true if the curve was a straight line; while in the case of the arc E and A may both vary with the current.

Mrs. AYRTON said that with reference to the question of the existence of a back E.M.F., the evidence tended to show that it did not exist. By using an exploring carbon no constant back E.M.F. could be found.

Prof. AYRTON said that, considering the arc as consisting of a back E.M.F. and a resistance, it was necessary to separate these two. Simply obtaining one value of the P.D. and the current was of no assistance in solving this question, but a series of values had to be taken. By taking the changes in the P.D. and current sufficiently small, the curve over the range considered was practically straight. It was curious to note that as long as observers obtained a positive value for the resistance of the arc, no fault was found with the method; but that now a negative value was found, the accuracy of this method was questioned. If a back E.M.F. does really exist, then it follows that the arc must have a negative resistance. Mr. Frith has shown why some people have got positive and some negative values for the resistance of the arc, and also that with an alternating current you may get either one or the other.

Mr. S. CARTER asked if the fact that the arc had a negative resistance did not imply a back E.M.F. in order that the arc might be stable. If so, was a negative resistance such an absurdity?

Mr. CAMPBELL said that he was very pleased to see that the authors had applied a method which he (Mr. Campbell) had suggested for measuring pulsating currents. If a pulsating current, such as could be obtained by means of a make and break, were passed through a thermopile you would get a back E.M.F., while if an alternating current were employed, you would not.

Mr. FRITH, in his reply, said that he had defined the "true resistance" as $\frac{dV}{dA}$. Mrs. Ayrton has shown that an arc will not run unless a certain resistance is placed in series with it; this resistance must be numerically equal to the negative resistance of the arc itself.

Prof. AYRTON said Mr. Frith's remarks as to the cause

of the want of stability of an arc without outside resistance were most suggestive.

The Chairman (Captain ABNEY) said he did not like the expression P.D. He suggested the employment of photography to facilitate the accurate registration of the instrument readings.

The further discussion on the paper was adjourned till the next meeting, on May 22nd.

NOTICES OF BOOKS.

Foods; their Composition and Analysis. A Manual for the use of Analytical Chemists and others. With an Introductory Essay on the History of Adulteration. By ALEXANDER WYNTER BLYTH, M.R.C.S., F.I.C., F.C.S., &c., Barrister-at-Law, Public Analyst for the County of Devon, and Medical Officer of Health and Public Analyst for St. Marylebone. With numerous Tables and Illustrations. Fourth Edition, Revised and Enlarged. London: C. Griffin and Co., Ltd., Exeter Street, Strand. 1896. 8vo., pp. 735.

A new edition of Mr. Wynter Blyth's standard work on Foods and their Adulteration, enriched, as is the one before us, with the recent discoveries and improvements effected in all civilised countries, will be accepted as a boon by public analysts and medical practitioners.

The history of the sophistication of food in the days of classical antiquity, in the Middle Ages, and even in later days, shows that the "good old times" had their shadow side, grim enough to all intents and purposes. We are apt to shudder on learning that at one time the bake-houses were used as a suitable place for disposing of the bodies of murdered persons. But we do not find that until recently sophistication was formally defended by persons of eminence—or at least of prominence—as being merely one form of the worship of the modern idol Competition. Some of the punishments inflicted of old for the adulteration of food certainly did not err on the side of leniency. Thus at Nuremberg, in 1444, one Jobst Fendeker was burnt for the crime of selling spurious saffron, and in the following year two men and a woman were buried alive for the same offence. In this country we should be very tolerant towards adulteration if it were limited to an article so utterly unimportant.

After the history of this rampant form of crime, we come to a view of the present state of the law in England relative to the adulteration of food, the text of the Acts of 1875 and 1897 being given in the Appendix. A careful perusal of these Acts leaves on the mind a very unsatisfactory impression. The punishments for the convicted offender—fines only—are often so low that the dealer may be quite willing to incur them for the sake of the additional gain. Repeated offences may be regarded as misdemeanours, and may be visited with imprisonment and hard labour. This penalty, though often justly incurred, is scarcely ever inflicted.

A great defect in the law as it stands is that, whilst it is invariably laid down that the money penalty inflicted in any case shall not exceed x pounds, there is no proviso against its being reduced to a merely nominal amount. Instances of this kind are too common. The quibble based on the words "to the prejudice of the purchaser," which seem to have been introduced for the very purpose of stultifying the Act, seems to have been at last got rid of. Section 5, which makes guilty knowledge essential to the proof of the offence, is another capital flaw. It may be fairly assumed that every dealer should be able to judge of the articles which he keeps for sale. If a retailer proves, to the satisfaction of the Court, that any article concerning which question has arisen is in the same state as supplied to him by a merchant or manufacturer, the law ought to see to it that the latter receives a heavier sentence.

A useful feature of this work is that due attention is called to the use of the spectroscope in the recognition of colouring-matters. In a note the author quotes, from the *Berichte*, that magnesium salts alter, more or less characteristically, the spectrum of juice of elder-berries, the colouring-matters of the beet, dahlia, dragon's mouth, horse-chestnut, hyacinth, rhododendron, purple aster, and *Primula farinosa*.

The examination of the "ash" of foods receives a very thorough notice. The author recommends that in all cases the percentage should be determined; in such fluids as milk, the alkaline phosphates and the chlorides; in seeds like wheat and cocoa, total phosphoric acid; in beer-ash, common salt; in bread ash, presence or absence of alumina, magnesia, and proportion of silica to alumina; in tea-ash, the alkalinity, and iron, silica, and proportion of soluble to insoluble ash; and in coffee-ash, the presence or absence of silica.

The old method of determining carbon dioxide by estimation, in light glass vessels, by loss of weight, is declared to be quite forsaken.

For total nitrogen in foods the Kjeldahl process is said to be now in most frequent use.

The newest fraud in sugars is to colour inferior qualities with yellow aniline dyes, and pass them off as Demerara. Beet sugars may be distinguished from cane sugars by a comparison of the ash, which in the former contain nearly thirteen times more soda than the latter. Among sweet-meats, toffy is correctly said to be composed of butter and sugar melted together. "Butter Scotch" is probably the same article under a new name. It is rightly remarked that beet-treacle has so unpleasant a taste that it is not used in articles of food.

For the recognition of alum in flour the work before us recommends Cailletet's "chloroform" test; but to distinguish between alumina derived from alum from such as may have been introduced as clay, the logwood test plays an essential part. Alum in food in "reasonable quantities" (what are they?) is pronounced not injurious to health.

It is not sufficiently known that in putrid peas there may be generated a peculiar poison, probably a ptomaine.

Peas preserved by the addition of copper have been found to be dangerous.

Coffee has been, almost from its first introduction into Europe, a favourite mark for sophistication, and so it still continues. The present law may be unfortunately evaded by calling the article "French coffee," "Coffee as in France," or some other such name. The gross mendacity of these names will appear if we remember that in France the consumer buys his coffee unground, often indeed unroasted, and, if he prefers the use of chicory, he buys this latter product separately, and adds it to the coffee in whatever proportion he desires. It was a step in the wrong direction when in England grocers were permitted to sell the two articles in mixture but were not required to state the proportions. Some years back a patent was actually granted for the manufacture of a spurious coffee with three parts of dates roasted up with one-third their weight of coffee. The odour, the flavour, and the physiological action of coffee are entirely wanting. The vilest fraud, however, is the manufacture of spurious coffee berries. Hence the consumer can no longer protect himself by buying his coffee unground.

Two additions to the Sale of Food and Drugs Act are here urgently needed. Firstly, if the word coffee occurs in the name of any substance offered for sale, it shall be amenable to the law just as if it were called coffee simply. Secondly, it should be enacted that any person who designs, makes, sells, or offers for sale, or uses any machine, stamp, or die, by which any paste, pulp, or powder can be pressed into the shape of coffee-berries, nutmegs, gall-nuts, peppercorns, or any other seed, nut, fruit, or berry occurring in commerce, every such person shall pay a penalty of not less than £200, and every such machine, stamp, mould, or die shall be destroyed, and, further, that

no letters patent shall be granted for the production of any alleged substitute for any article of food.

The reader will perceive that many adulterants formerly used or suspected are no longer met with. The chemical student and the practising analyst will find Mr. Blyth a safe guide in this difficult subject.

Alembic Club Reprints. The Liquefaction of Gases. Papers by MICHAEL FARADAY, F.R.S. (1823—1845). With an Appendix consisting of Papers by THOMAS NORTHMORE, "On the Compression of Gases" (1805—1806). Edinburgh: Wm. F. Clay.

The liquefaction of gases must certainly rank among the most momentous pieces of chemical work conducted during the present century. Scarcely had the idea of a gas been distinctly grasped when the question arose whether certain bodies, simple or compound, were essentially gaseous, or whether this condition did not depend on temperature and pressure. In early memoirs we read of "permanent gases," distinguished from vapours and from gases which could be liquefied.

It is not shown in these papers that Faraday was the first to effect the liquefaction of gases. On the contrary, he shows that, as early as 1797, Rumford had condensed carbonic acid. Guyton de Morveau had attempted the liquefaction of ammonia, but with very doubtful success. Sulphuric acid was liquefied by Monge and Clouet, and hydrogen arsenide by Stromeyer, as long ago as 1805. Chlorine seems to have been really liquefied by Northmore, but with hydrochloric acid his success was doubtful. Carbonic acid was probably liquefied by Babbage about 1813.

But the liquefaction of gases was first taken up systematically, and with a full account of the procedures employed, by Faraday, as shown in a paper read before the Royal Society, January 9th, 1845. He was successful with carbonic acid, hydriodic acid, hydrobromic acid, silicon fluoride, boron fluoride, muriatic acid, sulphurous acid, hydrogen sulphide, carbonic acid, euchlorine, nitrous oxide, cyanogen, ammonia. Seven of these substances—including ammonia, nitrous oxide, and sulphuretted hydrogen—were solidified. Hydrogen, oxygen, nitrogen, nitric oxide, carbonic oxide, and coal gas could not be liquefied by the resources at Faraday's disposal.

It is exceedingly interesting that in the same laboratory—that of the Royal Institution—where Faraday's researches were carried on, Professor Dewar has latterly liquefied oxygen, hydrogen, and nitrogen in considerable quantities, thus putting the finishing stone on Faraday's work and effacing the class of supposed "permanent gases." Faraday's experiments must always attract attention for their simplicity and beauty.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 17, April 27, 1896.

Method of Action of the X Rays on the Photographic Plate.—R. Colson.—The author investigates if the X rays act upon the photographic plate directly or by the intermediary of a transformation. His experiments seem to him to favour the former supposition.

The Heterogeneity of the Radiations emitted by Crookes Tubes, and on their Transformation by Screens.—F. Le Roux.—The photographic impressions produced by the Crookes tubes have, in the author's opinion, two principal causes, the radiations emitted by the surface of one or other of the electrodes and those

emanating from the wall of the enclosure rendered phosphorescent.

Action of the X Rays on Electrified Bodies.—L. Benoist and D. Hurmuzescu.—Not adapted for useful abridgment.

On the Rays of Röntgen Electrified.—A. Lafay.—The study of the phenomena of the charge and the discharge of conductors of the Röntgen rays presents causes of error which it is very difficult to avoid absolutely. We see especially that the charge cannot exceed a certain limit in value, which depends on the form of the conductor, on its nature, and on its position within the protective enclosure.

Optical Superposition of Six Asymmetric Carbons in one and the same Active Molecule.—Ph. A. Guye and Ch. Goudet.—The authors hold that the study of amyl-divaleryl tartrate, affording an instance of the algebraic superposition of the optical actions of six asymmetric carbons in one and the same active molecule, completes demonstration of the principles which they laid down at the outset of their researches, the independence and the algebraical superposition of the optical effects.

New Basic Magnesium Nitrate.—Gaston Didier.—This compound has the composition $3\text{MgO} \cdot \text{N}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$. It is rapidly destroyed by cold water.

On Crystalline Iron Sesquiphosphide.—A. Granger.—This substance has the composition Fe_2P_3 . It is insoluble in nitric and hydrochloric acid and in aqua regia. At a bright red heat it loses phosphorus, and melts with difficulty.

A Study on Peridinitronaphthalene.—Ch. Gassmann.—An energetic nitration of naphthalene produces two new bodies, α and β binitronaphthalene, fusible at 170° . The two dinitronaphthalenes separated by means of acetone.

On Phenylhydrazine Tartrate and its Derivatives.—H. Causse.—The author has obtained a bitartrate, $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_{12}$, a double phenylhydrazine-potassium bitartrate, a double phenylhydrazine-barium compound, and a double phenylhydrazine and antimony compound.

Combustion-heat of the Cyanogen Derivatives.—M. Guinchant.—The author's results are given in the form of tables.

Distillation of the First Acids of the Fatty Series.—E. Sorel.—I have been induced to apply to mixtures of water with the first four acids of the fatty series the method of distillation by successive fractions sheltered from radiation, as I have described in the *Comptes Rendus*, cxvi., p. 693. I have operated this time in a glass flask with a curved neck plunged into a double enclosure. The neck of the flask, bent at an acute angle, traverses a copper lid lined with asbestos, so that any return of the condensed product to the body of the flask is impossible. The outer enclosure, raised by a ring of gas-burners to a temperature higher than the ebullition point of the liquid in question, gradually heats the internal enclosure in which is the flask containing 550 c.c. of the liquid being studied, and when a thermometer placed close to the neck and the body of the flask showed a temperature at least equal to that of ebullition I light a Bunsen burner under the flask and conduct the distillation slowly. The condensed liquid is collected by fractions of 50 c.c. We thus know the composition of the liquid in the flask at the moment of collecting each fraction. We put aside the first 50 c.c., which may in part have been distilled below the normal temperature of distillation. The results are given in tables.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxiii., No. 3.

Detection of Silver and Gold in Iron.—H. N. Warren.—From the CHEMICAL NEWS.

MISCELLANEOUS.

The Sanitary Institute.—The Council have accepted an invitation from the city and county of Newcastle-upon-Tyne to hold a Sanitary Congress and Health Exhibition in that city in the autumn of this year.

The South African Horse Sickness.—According to a medical contemporary, Dr. Erdington, the Director of the Cape Town Bacteriological Institute, has detected the microbe occasioning the horse-disease of South Africa. Its identification was easy, but its culture was very difficult. The gum of the wild mimosa is laden with the *Mycelia*. As the disease is a great obstacle to the development of valuable tracts of land, Dr. Erdington recommends the destruction of the mimosa trees.

Royal Institution.—The Annual Meeting of the Members of the Royal Institution of Great Britain was held on the 1st inst., Sir James Crichton-Browne presiding. The Annual Report of the Committee of Visitors for the year 1895, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The real and funded property now amounts to above £100,000, entirely derived from the contributions and donations of the Members and of others appreciating the value of the work of the Institution. Seventy-two new Members were elected in 1895. Sixty-three lectures and nineteen evening discourses were delivered in 1895. The books and pamphlets presented in 1895 amounted to about 260 volumes, making, with 594 volumes (including periodicals bound) purchased by the Managers, a total of 854 volumes added to the library in the year. Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year. The following gentlemen were unanimously elected as officers for the ensuing year:—**President**—The Duke of Northumberland, K.G. **Treasurer**—Sir James Crichton-Browne, M.D., F.R.S. **Secretary**—Sir Frederick Bramwell, Bart., D.C.L., F.R.S. **Managers**—Sir Frederick Abel, Bart., K.C.B.; Sir Benjamin Baker, K.C.M.G.; John Wolfe Barry, Esq., C.B.; The Right Hon. Lord Halsbury; Charles Hawksley, Esq., M.Inst.C.E.; John Hopkinson, Esq., F.R.S.; Victor Horsley, Esq., F.R.S.; William Huggins, Esq., F.R.S.; The Right Hon. Lord Kelvin, F.R.S.; Alfred B. Kempe, Esq., F.R.S.; George Matthey, Esq., F.R.S.; Ludwig Mond, Esq., F.R.S.; Sir Andrew Noble, K.C.B., F.R.S.; The Right Hon. Earl Percy; Basil Woodd Smith, Esq., F.R.A.S. **Visitors**—Gerrard Ansdell, Esq., F.C.S.; Sir James Blyth, Bart.; Arthur Carpmal, Esq.; Sir William James Farrer, M.A., F.S.A.; Carl Haag, Esq., R.W.S.; Sir Francis Laking, M.D.; Hugh Leonard, Esq., M.Inst.C.E.; James Mansergh, Esq., M.Inst.C.E.; Lachlan Mackintosh Rate, Esq., M.A.; Felix Semon, M.D., F.R.C.P.; Henry Virtue Tebbs, Esq.; John Isaac Thornycroft, Esq., F.R.S., M.Inst.C.E.; Thomas Tyrer, Esq., F.C.S., F.I.C.; John Westlake, Esq., Q.C., LL.D.; James Wimshurst, Esq.

MEETINGS FOR THE WEEK.

- TUESDAY, 26th.**—Royal Institution, 3. "The Building and Sculpture of Western Europe," by Prof. T. G. Bonney, F.R.S.
— Medical and Chirurgial, 8.30.
— Photographic, 8.
WEDNESDAY, 27th.—British Astronomical, 5.
— Geological, 8.
THURSDAY, 28th.—Royal Institution, 3. "Lake Dwellings," by R. Munro, M.D., M.A.
— Chemical, 8. "Lothar Meyer Memorial Lecture," by Prof. P. Phillips Bedson, D.Sc.
— Institute of Electrical Engineers, 8.
FRIDAY, 29th.—Royal Institution, 9. "John Wesley—Some Aspects of the Eighteenth Century," by Augustine Birrell, Q.C., M.P.
SATURDAY, 30th.—Royal Institution, 3. "The Moral and Religious Literature of Ancient Egypt," by Dr. E. A. Wallis Budge, M.A.

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SESSION 1896-97.

The Courses of Instruction in ENGINEERING and CHEMISTRY at the Institute's Colleges commence in October, and cover a period of two to three years. The MATRICULATION EXAMINATION of the CENTRAL TECHNICAL COLLEGE will be held on September 21st to 24th, and the ENTRANCE EXAMINATION of the DAY DEPARTMENT of the TECHNICAL COLLEGE, FINSBURY, on September 22nd.

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Professors:—O. HENRICI, LL.D., F.R.S. (Mathematics), W. C. UNWIN, F.R.S., M.I.C.E. (Civil and Mechanical Engineering), W. E. AYRTON, F.R.S. (Physics and Electrical Engineering), H. E. ARMSTRONG, Ph.D., F.R.S. (Chemistry).

CITY AND GUILDS TECHNICAL COLLEGE, Finsbury (Leonard Street, City Road, E.C.). The DAY DEPARTMENT provides Courses of Intermediate Instruction for Students not under 14 years of age, preparing to enter Mechanical or Electrical Engineering and Chemical Industries.

The ENTRANCE EXAMINATION will be held on September 22nd, and the new Session will commence on October 6th.

Professors:—S. P. THOMPSON, D.Sc., F.R.S. (Electrical Engineering), J. PERRY, D.Sc., F.R.S. (Mechanical Engineering), R. MELDOLA, F.R.S. (Chemistry).

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1905.

ON THE AMOUNT OF ARGON AND HELIUM CONTAINED IN THE GAS FROM THE BATH SPRINGS.*

By Lord RAYLEIGH, Sec. R.S.†

THE presence of helium in the residue after removal of nitrogen from this gas was proved in a former paper (*Roy. Soc. Proc.*, lix., p. 206, 1896), but there was some doubt as to the relative proportions of argon and helium. A fresh sample, kindly collected by Dr. Richardson, has therefore been examined. Of this 2500 c.c., submitted to electric sparks in presence of oxygen, gave a final residue of 37 c.c., after removal of all gases known until recently. The spectrum of the residue, observed at atmospheric pressure, showed argon, and the D_3 line of helium very plainly.

The easy visibility of D_3 suggested the presence of helium in some such proportion as 10 per cent, and this conjecture has been confirmed by a determination of the refractivity of the mixture. It may be remembered that while the refractivity of argon approaches closely that of air, the relative number being 0.961, the refractivity of helium (as supplied to me by Professor Ramsay) is very low, being only 0.146 on the same scale. If we assume that any sample of gas is a mixture of these two, its refractivity will determine the proportion in which the components are present.

The observations were made by an apparatus similar in character to that already described, but designed to work with smaller quantities of gas. The space to be filled is only about 12 c.c., and if the gas be at atmospheric pressure its refractivity may be fixed to about 1/1000 part. By working at pressures below atmosphere very fair results could be arrived at with quantities of gas ordinarily reckoned at only 3 or 4 c.c.

The refractivity found for the Bath residue after desiccation was 0.896 referred to air, so that the proportional amount of helium is 8 per cent. Referred to the original volume, the proportion of helium is 1.2 parts per thousand.

A GENERAL VOLUMETRIC DETERMINATION OF THE METALS PRECIPITABLE BY FIXED CAUSTIC OR CARBONATED ALKALIS.‡

By Prof. Dr. RUOSS.

THIS method presupposes that the metals precipitable by alkaline hydroxides or carbonates have been so far separated that only one of them is present in a solution.

Such a solution is in the first place rendered exactly neutral, so that no more free acid is present. This can be quite accurately effected with methyl-orange, even in neutral salts which have an acid reaction with litmus, such as, e.g., copper sulphate, zinc sulphate, iron sulphate, alum, &c., on the condition that acetic acid or oxalic acid is not present. In many cases, on the transition from free acid to perfectly combined acid, methyl-orange shows a change of colour, from rose to yellow, which takes place abruptly; but, as Thomson has previously shown,

this does not occur in all cases. Thomson then recommends to assume as the final point of the neutralisation the moment when a decided change of colour ensues.

I shall show that this assumption is not incontrovertible, and gives occasion for various errors.

According to Thomson's researches, 50 c.c. of normal lye required 49.95 c.c. of normal sulphuric acid until the pale yellow colour changed to a perceptible red; at 50 c.c. there occurred a distinct change to red, which, however, develops its full intensity only at 50.15 c.c. As sodium sulphate mixed with methyl-orange has a pale yellow colour, the true colour at 49.95 is pale yellow, not reddish. The latter colour is, in fact, not permanent, and if the liquid at 49.95 is heated and cooled the pale yellow colour becomes distinct. I regard it as absolutely necessary when the liquid is near the neutral point to heat and then to cool. To me, the titration method does not seem sufficiently accurate for the study of the changes of colour. Chemically pure salts, free from acid, which are mixed with alkali or acid give more accurate starting-points. The salts obtained by re-crystallisation mostly contain free acid; thus, e.g., pure zinc sulphate colours methyl-orange a rose. If the free sulphuric acid (which adheres most obstinately to zinc sulphate) is expelled by evaporation to complete dryness, it colours methyl-orange a pale yellow.

The conception of decided changes of colour is very indefinite, and from Section 16 of Thomson's memoir (*Zeit.* xxiv., p. 222) it appears that there exist inaccurate titrations.

Thomson there arrives at the result:—With methyl-orange the alumina present is almost entirely conjointly titrated.

By warming and cooling there would be, not 5.7, but 6 c.c.; that is, the entire alumina.

It is a rule to titrate with methyl-orange only in the cold, but by comparing the colour in a hot solution with that in a cooled solution, we arrive—even in cases otherwise doubtful—at a sharp determination of the end of the titration. We divide the salts into two groups as regards their behaviour with methyl-orange:—

1. Salts which give a yellow colour in a neutral solution;
2. Salts which give an orange colour in a neutral solution.

The first group comprises the majority of all salts; in them, in the transition from acid to neutral, there occurs a change from rose at once to a pale yellow, and from rose by way of orange into yellow.

The orange colour, on heating, changes to yellow, and on cooling returns to an orange.

The second group comprises only a few salts which, in a neutral solution, have a strongly acid reaction with litmus, e.g., alum.

On the transition from acid to neutral, there appears merely a change from rose to orange. On heating, the orange colour is permanent or changes to a red.

In order to neutralise an acid solution, we add alkali until the red changes its colour, and we have then to note three phenomena:—

1. Red changes to pale yellow; the solution is then neutral.
2. Red turns to orange, and, on heating, the orange to a yellow.

Alkali is then added drop by drop to the cold solution till this likewise is yellow.

3. Red turns to orange; but this orange does not change to yellow on heating. The solution is then neutral.

Some examples may explain these differences.

We add to a solution of magnesium sulphate in a test-glass one drop of acid and methyl-orange (of a solution containing one grm. of the indicator per litre, we take to 100 c.c. of liquid two to four drops); we heat and cool

* A Paper read before the Royal Society, May 21, 1896.

† I am reminded by Mr. Whittaker that helium is appropriately associated with the Bath waters, which were called by the Romans *Aquæ Solis*.

‡ *Zeitschrift für Analytische Chemie*.

by immersing the lower part of the glass in cold water; the upper (hot) part of the liquid is then yellow, and the lower (cold) part is orange to red. The same takes place also in cold solutions, such as dilute solution of copper sulphate; though here the difference of colour in the hot and cold liquid cannot be mistaken.

A solution of alum, to which has been added a drop of alkali and methyl-orange, appears orange, and on heating does not change to a yellow. With a drop of acid, we have a rose colour in the cold solution.

In many cases we can, from an acid metallic solution, obtain a neutral liquid by evaporating to dryness with sulphuric and nitric acid and dissolving the residue in water.

As a further indicator we use phenolphthalein. Its application depends on the following:—

If we mix a metallic solution with phenolphthalein and add alkalis (caustic or carbonated), the phenolphthalein does not show an alkaline reaction until all the metal has been precipitated. Ebullition is generally necessary.

The quantity of the metal present is then calculated from the quantity of alkali which has to be added to the metallic solution from the neutral point until the phenolphthalein turns red.

It would be a waste of time if we were to titrate to the exact point where the phenolphthalein turns red. We therefore add more alkali than is necessary, and remove the excess by adding acid until the solution is colourless. This method requires its justification; for on the addition of the acid it might dissolve the precipitate instead of neutralising the alkali of the supernatant liquid. The purpose of the addition of the acid is that one equivalent of acid neutralises one equivalent of alkali; if this does not take place, and if the equivalent of acid dissolves one equivalent of the precipitate, this equivalent of dissolved precipitate neutralises in turn one equivalent of alkali, and forms with it an insoluble precipitate. In one or other manner, one equivalent of alkali is always neutralised by one equivalent of acid.

As regards the addition of phenolphthalein, we take an arbitrary quantity; since this quantity is not taken into consideration, as the final reaction requires the indicator to be colourless.

Methyl-orange is decomposed in boiling nitric acid; hence, on neutralising, we add, if free nitric acid is present, alkali until precipitation takes place. This precipitate is then removed by the addition of dilute hydrochloric or sulphuric acid.

The details of the process can be inferred from the following examples:—

I.—Precipitation of the Metals as Oxides.

1.0993 grms. of copper sulphate was dissolved in water in a beaker glass, and phenolphthalein was then added.

One-fifth normal soda-lye was then added until the greenish blue colour passed, at 37 c.c. of lye, to a dark violet-blue. The liquid was then boiled; there was formed a black precipitate, and on removing the source of heat the supernatant liquid was colourless. After adding a further c.c. of lye, the supernatant liquid after ebullition was again colourless. We proceed further by c.c.'s until, after the addition of 45 c.c. of lye, the supernatant liquid was *intensely* red—a colour which did not disappear on prolonged ebullition.

Into the hot solution, after the subsidence of the precipitate, one-fifth normal sulphuric acid was then run drop by drop (the quantity being at most 1.5 c.c.). With each drop the liquid was gently agitated. Without any unusual skill it is practicable to effect this rotatory agitation so that the precipitate remains as far as possible at rest. Hence the precipitate does not need to be allowed to settle in order to judge of its colour. A white paper placed a few c.c. below the beaker renders it easy to decide on the colour.

After the addition of 0.8 c.c., sulphuric acid had dis-

appeared. Hence 44.2 c.c. of lye were necessary, and the quantity of copper sulphate was, therefore,—

$$44.2 \cdot 24.88 \text{ m.grms.} = 1.0997 \text{ grms.}$$

The precipitate was then dissolved in nitric acid, mixed with soda in a solid form until a slight precipitation ensued, boiled, and the precipitate was removed with one-fifth normal sulphuric acid.

Methyl orange was then added, and the liquid cooled. Soda-lye was then run in, with circular rotation after each drop, until the red colour turned to an orange. It was heated, and as, after cooling, the colour was yellow, it was neutral.

Now the actual titration commenced, proceeding as above; 44.2 c.c. of lye were used.

With the colours red and yellow we cannot, of course, speak of pure red and yellow, but of a mixed colour between these and the colour of the dilute copper solution.

It would, of course, have been simpler to evaporate the solution to dryness with sulphuric and nitric acid, to take up the neutral residue with water, and to titrate with phenolphthalein and soda-lye. But I sought to show that the neutralisation might also be effected in another manner.

It is not admissible to assume the neutral point on the occurrence of a minimal precipitate; such minimal precipitates disappear on heating, and often correspond not even to one drop of one-twentieth normal solution.

It was also attempted to carry out the determination of copper in a cold solution. It appeared thereby that the liquid standing above the voluminous precipitate of copper hydroxide became red long before the end of the titration, and an examination of the precipitate showed that it contained undecomposed copper sulphate. However, it is possible, with precipitates of small volume and with vigorous agitation, to effect the titration in the cold.

II.—Precipitation of the Metals as Carbonates.

We have here to take the circumstance into account that the carbonates are somewhat soluble even in pure water, and hence colour phenolphthalein reddish.

Thomson in his investigations arrived at the result that boiled barium or calcium carbonate is neutral to this indicator.

If we mix a solution of soda with an excess of barium or calcium chloride, add phenolphthalein, and boil for about five minutes, the liquid has a faint reddish colour, which in large strata is distinctly red against a white back-ground.

This circumstance is in part the cause that Thomson's proposed determination of lime and baryta yields no useful results.

An excess of soda is needed for complete precipitation, and on ebullition the red colour appeared long before complete precipitation.

We again added an excess of soda, and may take two ways for the neutralisation of the excess of alkali.

1. We use Warden's method (*American Chemical Journal*, iii., 1).
2. We filter, and in the filtrate we determine the excess of carbonate by acid.

The first-mentioned method is the simpler. After boiling, we allow the liquid to cool and deposit, stirring very gently, and adding drops of acid with a glass rod until the red colour disappears. The double quantity of acid is then deducted.

(The applications of the method will follow).

(To be continued).

Novel Mode of the Synthetic Preparation of Urea and of the Compound Symmetrical Ureas.—P. Cazeneuve.—The author regards guaiacal carbonate as a fruitful and interesting agent for the production of new symmetrical ureas.—*Comptes Rendus*, cxxii., No. 18.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 242).

I CHECKED the electric spectrum of thallium shown by the thallous sulphate and chloride prepared from purified Lamy's sulphate, by using successively *sulphate, chloride, bromide, iodide, carbonate, and nitrate*, prepared by myself, thallium sent me by Mr. Crookes, and thallium that I had bought. When using these compounds in a perfectly pure state I saw exactly the same spectrum, consisting of a single green line. It was the thallous nitrate, formed by dissolving the metal produced by electrolysis in nitric acid, only just distilled in platinum, which showed the electric spectrum, consisting of a single line, the most rapidly, the most surely, and with the greatest colour intensity. The luminosity was so great that it was necessary to make the slit very narrow, so as to shut off a partial continuous spectrum, and especially to use a vertical spark. By causing the spark to impinge on a solution newly made by the action of nitric acid on the metal, one is certain to obtain the single green thallium line, without either a continuous spectrum or air lines, or any other line. When using thallous nitrate containing a small quantity of nitrate of silver, the single thallium line was again seen. The characteristic silver lines were absent. As regards the electric spectrum of *metallic thallium*, I carried out the following experiments:—

After having completely coated with pure fused thallium either small platinum balls or small pointed cones of pure carbon, recently heated and held in a thick platinum wire, I arranged them *horizontally*, 2 or 3 m.m. apart, in front of the slit of the Steinheil spectroscope, and passed in succession an *induction spark, a discharge, or a current from a battery*, capable of forming after previous contact an arc equal in length to the distance between the two points, that is 2 or 3 m.m.

Spectrum analysis of the *spark or discharge* showed the green thallium line, together with a very faint sodium line on a dark background, *free from or accompanied by air lines*, according to the relative intensity of the spark or discharge.

In the spectrum formed by analysis of an electric arc, I saw the thallium line very brilliantly coloured, as well as a *weak sodium line*, but no trace of air or any other lines, whatever the *intensity and direction* of the current might be.

At the time these experiments were made, spectrum analysis of a strong spark enabled me to see a very brilliant sodium line in the spectrum, side by side with air lines.

Thus, *in air*, the electric spectrum of metallic thallium is the same as that of the chloride, oxide, sulphate, nitrate, &c., of this metal. As chloride, nitrate, and sulphate of thallium are dissociated in the spark, and form in this case black oxide of thallium, one may ask whether, when working in air, one really sees the spectrum of the metal, and not that of its oxide.

I made experiments on this point, working in a hard glass tube full of pure hydrogen, 10 c.m. long by 4 c.m. diam. I took care to heat, in a current of hydrogen, either thallium fused and cast into pointed cylinders, or thallium adhering to platinum balls or cones of pure carbon, so as to make the metal very bright, and surround the thallium by free hydrogen. As regards the thallium spectrum, the result was the same; I found, in fact, that with a weak spark the spectrum contained a single green line. *Neither the sodium nor any other line was seen.* The spectrum from *strong discharges* showed *three lines*; one sharp pale red line at division 36; the pure and brilliant green thallium line at 65.5; and a hazy, very pale bluish green line at 85.0 on the Steinheil spectroscope. Now the lines at 36.0 and 85.0 correspond to Fraunhofer's C

and F lines; they were due to the hydrogen in which the discharge took place. Having noted these facts, I looked for the blue line at 118.6, also belonging to hydrogen, but in vain, even when changing the analyser and the direction of the current.

When using the Hilger spectroscope, with its six prisms, spectrum analysis of a *weak or strong electric arc*, passing between carbon cones coated with thallium, only showed the single thallium line, although I had thus passed into the hydrogen a sufficient amount of thallium vapour to *rapidly cover* the upper part of the tube used as a reservoir with a very bright metallic coating, and in a very short time make the sides of the tube opaque.

In the spectrum of a thallic electric arc from a battery of thirty very large Bunsen cells, the intensity of the green line was very much weakened by the luminosity of the background, due to the production of a bright continuous spectrum. In order to see the line properly, I had to narrow the slit until it was almost closed. The luminosity of the background greatly exceeded that, although so great, noticed in the spectrum of thallium vapour raised to the fusing-point of iridium in an oxy-hydrogen blowpipe. *Hydrogen and other lines can therefore exist without the eye being able to detect their presence.* I can only compare the luminosity of the spectrum of a thallic voltaic arc to the luminosity seen when directing the collimator of a spectroscope of *low absorption power to the surface of the sun*. In fact, under these conditions, when using the Steinheil spectroscope, I was unable to see the Fraunhofer lines, however narrow the slit might be.

When testing, under these conditions, the possibility of observation BY THE EYE, I ought to mention that the electric spectrum of thallium consists of *a single line not capable of being split up*, exactly like the flame spectrum of this metal, and that *electricity is no more capable of dissociating it than heat*.

Since observers have found a complex electric spectrum of thallium when using thallium they have not prepared themselves, I think I am correct in concluding that the metal they used was other than that used by Bunsen, Lecoq de Boisbaudran, and myself.

There remains the description of the experiments I made to ascertain whether the position of the thallium line was the same in the flame and electric spectra.

On the Position of the Thallium Line in the Flame and Electric Spectra.

In his "Spektal-analytische Untersuchungen," M. Bunsen, whose work I have taken as a basis of comparison, because, amongst other reasons, I have a spectroscope exactly like his, assigned to the thallium line in the flame and electric spectra a difference in position amounting to 0.6 micrometer division on the luminous projection of his instrument. In fact, between the position of the centre of the sodium line in flame and electric spectra, the tables show a difference of 0.5 division. This difference is at least double the mean error admissible in measuring the position of a line in the electric spectrum, when using a micrometer with a luminous projection. I tried to find out whether this difference was due to an error in observation, or whether, in spite of the singleness of the line, the positions of the thallium line in the flame, spark, and electric arc spectra were not the same. To solve this question, I started the experiments I am about to describe.

As regards the flame spectrum of thallium, the mobility of which is great, I was soon convinced that by introducing thallium, or one of its compounds, into a hydrogen or Bunsen flame placed in front of the collimator, an error might be made amounting to 0.75 division on the luminous projection, according to the position of the flame in front of the collimator and the part of the flame into which the thallium was introduced. This may be observed whether the centre of the line is found by bringing the cross wires alternately from right to left and

from left to right of this centre, according to M. Lecoq de Boisbaudran's advice, or whether it is *estimated*, as those do who, when *weighing*, instead of balancing exactly by the *addition of weights*, judge of the oscillations about zero by the position of the pointer of the balance when it stops momentarily.

According to my lengthy experience, this system admits of readings being taken exact to *one-tenth*, and with practice to one-twentieth, of a scale division, though this division may be only about 1 m.m. I constantly use this method of reading, not only because of its rapidity, but especially because it dispenses with touching the lens of the spectroscope, any movement of which involves a risk of displacing the micrometer.

To obtain the greatest possible steadiness in the position of the thallium line, I was obliged to substitute for the flame of a lamp a blowpipe flame obtained by burning a mixture in proper proportions of coal-gas and air, separately stored under water in large quantities, under a constant pressure of from 2 to 3 c.m. of water, by means of the blowpipe used by Mr. Matthey for welding platinum.

On fitting a platinum nozzle with a hole about $\frac{1}{2}$ m.m. in diam., to the blowpipe, fitted with taps to regulate the supply of gas, it was possible to obtain at will a *vertical motionless* blowpipe flame (thanks to the use of screens), from 7 to 10 c.m. high and from 5 to 6 m.m. diam., coloured deep or pale blue, according to the volume of air mixed with the coal-gas in the blowpipe, and to the pressure under which the gases issued. I arranged the blowpipe on a stand with a rack, and put it on the left-hand board on the table carrying the spectroscope. I described this board in the Introduction to my "Spectroscopic Researches."*

The blowpipe was adjusted in front of the collimator so as to make the *right edge* of the flame coincide exactly with the axis of the collimator. I effected this adjustment by finding the position in which I could see a continuous spectrum appear on the background, on introducing a fine platinum wire into the blowpipe. Having adjusted the fiftieth division of the micrometer of the Steinheil spectroscope on Fraunhofer's D line, I put a point of the right edge in contact successively with thallium and the chloride, sulphate, and nitrate of this metal, on a fine platinum wire loop. I effected this contact by placing the carrier on the right-hand board, also described in the Introduction, by moving it slowly by means of its endless screw. The pitch of the screw being very fine, it is certain to penetrate into the flame only a fraction of a m.m. This slight penetration is necessary, on account of the extreme volatility of the metal and its compounds, in order to obtain a thin sheet of thallium vapour.

To eliminate any error due to the position of the blowpipe, I took the precaution of *displacing and replacing* the blowpipe and the carrier *after each measurement of position*, leaving the cross hairs in position. I could measure by *estimation* to from 0.05 to 0.10, the difference between the centre of the thallium line after the successive displacements and replacements. These movements could be made easily and quickly, thanks to the supports which moved by means of endless screws.

(To be continued).

Colorimetric Determination of Iron.—G. Lunge.—The author, for detecting traces of iron, especially in aluminium sulphates, makes use of the sulpho-cyanogen reaction. He transfers the iron sulpho-cyanide from the aqueous solution to one in ether, by shaking out the former with ether. It is found preferable to effect the peroxidation of the iron solution by potassium chlorate and hydrochloric acid instead of nitric acid.—*Zeit. für Angewandte Chemie.*

A REVISION OF THE ATOMIC WEIGHT OF ZINC.*

FIRST PAPER: THE ANALYSIS OF ZINCIC BROMIDE.

By THEODORE WILLIAM RICHARDS

and
ELLIOT FOLGER ROGERS.

(Continued from p. 241).

FINAL SERIES OF DETERMINATIONS.

By THEODORE WILLIAM RICHARDS.

One determination of the final series, No. 17, was made with the old zincic bromide in the new apparatus. The others were all made from new material prepared from electrolytic zinc and pure bromine, instead of from zincic oxide and hydrobromic acid. The electrolytic zinc was prepared with great care in the following manner:—An excess of "pure" zinc was treated with somewhat dilute pure sulphuric acid at 80° until, upon dilution, a marked amount of basic salt was formed. About 300 grms. of zinc had been dissolved; and this diluted solution was allowed to stand for many hours in contact with the zinc and the basic salt. After filtering, clear pieces of zinc were added to the solution; and no further metallic precipitate formed upon the zinc. The solution was then decanted and treated with a small amount of sulphuric acid and much hydric sulphide. After some time, the pure white precipitate was separated by decantation and filtration, and the solution was oxidised by an excess of pure chlorine. To this solution was then added enough very pure sodic carbonate to form a slight precipitate, and the mixture was allowed to stand several days with occasional stirring. The pure white precipitate, which must have contained any trace of iron remaining, was filtered off, and the sulphate of zinc was crystallised three times successively from hot water.

The solution of the last crystals was allowed to stand for two days over several grms. of the purest crystalline electrolytic zinc in a large platinum dish. At the end of that time the solution contained some basic salt, but the dish showed no sign of a metallic coating. The solution was filtered, treated with an excess of freshly distilled ammonia, and electrolysed. A thin rod of very pure zinc served as the negative pole, and a platinum wire as the positive. Six decomposing cells were run simultaneously on a shunt from a 50-volt dynamo which was being used for charging a storage battery. The current in each decomposing cell varied from 1 to 1 $\frac{1}{2}$ ampères—if a much stronger current were used the cells became too warm. As Ramsay and Reynolds (*loc. cit.*) have suggested, it is advisable to remove the remarkably beautiful crystals from time to time as they grow; for this purpose a bent five-pronged glass fork, made from a heavy rod, was found very useful. The crystals were washed with ammonia until the washings were absolutely free from sulphuric acid, then with pure very dilute hydrobromic acid, and finally with much pure water. About 40 grms. of pure zinc thus formed were treated with an excess of pure bromine, which had been shaken with an alkaline bromide in aqueous solution, dissolved in concentrated calcic bromide, precipitated by water, and distilled under dilute pure hydrobromic acid. The Jena glass flask in which the combination took place was cooled during the reaction. The red solution was filtered in a glass funnel through asbestos, and the excess of bromine, together with any trace of iodine which may have been present, was driven off by leaving the Jena flask upon the steam-bath for some time in a very much inclined position. The diluted colourless solution was evaporated to small bulk, and the greater part of it was subjected to fractional crystallisation by cooling to zero. A portion which had crystallised twice successively from water was labelled (A);

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*. Presented April 10, 1895.

and another portion, the extreme mother-liquor remaining from two crystallisations, was labelled (C). Sample (B), the intermediate fraction, was not used in these experiments, as (A) and (C) were proved to be identical.

Before analysis, both (A) and (C) were subjected either to distillation or to sublimation. The sublimation was carried on in the lower part of a platinum retort, to which had been fitted closely a glass adapter for conducting the current of pure dry carbon dioxide. The substance to be sublimed was contained in a small platinum crucible fitted with a wire handle, by which it could be easily raised, lowered, or removed. The adapter was so arranged that the current of gas came as closely as possible in contact with the crucible, and so that any zinc bromide which might condense in a liquid form upon the glass, and thus run the risk of taking alkali from it, must return to the

From the substance used in the preliminary determinations (Expt. 17)	65.410
From new substance, not crystallised from water, but distilled in carbon dioxide (Expt. 14) ..	65.403
From extreme mother-liquors from crystallisation (C) sublimed in carbon dioxide (Expt. 18) ..	65.404
From purest crystals (A), twice crystallised from water and sublimed (Expts. 15, 19)	65.404
From purest crystals (A), twice crystallised from water and twice distilled in carbon dioxide (Expt. 16)	65.398

Average Zn=65.404

the metal may be obtained in the purest possible state; for if it is distilled according to Stas there is always

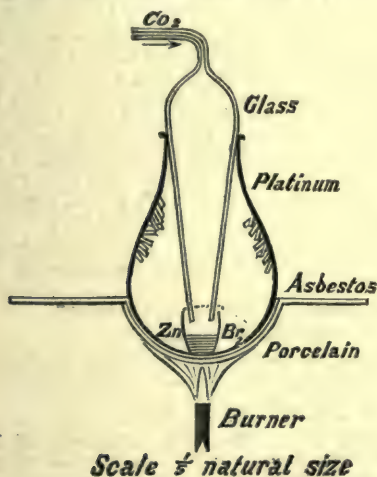


FIG. 3.

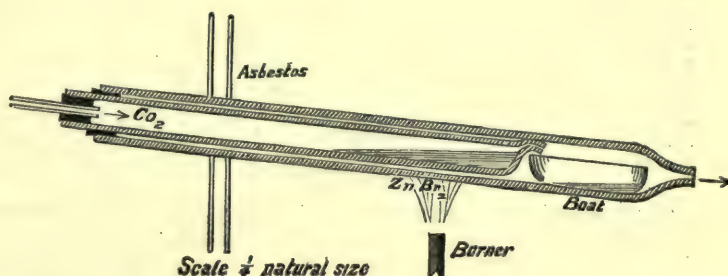


FIG. 4.

crucible and be re-distilled. The sectional drawing will give a clearer idea of the arrangement (Fig. 3).

Two powerful Bunsen burners supplied heat from below, impinging upon a porcelain dish which fitted closely to the bottom of the retort and protected the platinum. The gases from the flame were diverted by a large diaphragm of asbestos board. By means of this arrangement it is possible to sublime about half a grm. of zincic bromide an hour; the crystals are exceedingly beautiful, and give every evidence of great purity.

Instead of being sublimed, some of the pure salt was distilled in a current of carbon dioxide. For this purpose a medium sized tube of the hardest glass was drawn out so as to serve for a small retort, and this was encased in a larger hard glass tube, from which it was separated by several pieces of platinum foil. A platinum boat, into which was directed the drawn-out and turned-over point of the inner tube, served as the receiver. Here, again, a diagram must assist the explanation (Fig. 4).

The zinc bromide thus distilled possessed a peculiarly brilliant white lustre; in no case did the boat lose or gain the twentieth of a m.grm. in weight during the distillation.

The attempt was made also to distil the bromide in a vacuum, but the reduction of the pressure lowered the boiling-point too nearly to the proximity of the melting-point for convenient manipulation.

In this connection it may be well to state the atomic weight of zinc obtained from these specimens, in order to show their identity. The details of these figures are given later.

Silver.—The silver used in the final determinations was repeatedly purified by the methods already described. Finally, the beautiful electrolytic crystals were fused in a small crucible of pure lime in a vacuum. In this way

danger of impurity from the oxygen and illuminating gas or hydrogen used in the oxygen blowpipe.

Other Materials.—The acids were purified in the usual fashion and the greater part of the water used was only distilled twice, rejecting the first portions. For Experiment 16, all the water used was distilled three times, once over potassic permanganate. Of course, the platinum condenser which has been already described served for all of these distillations (*Proc. Amer. Acad.*, xxx., 380).

Phosphoric pentoxide was sublimed in a stream of pure oxygen. Since the presence of oxides of nitrogen in carbon dioxide might assist the partial decomposition of zincic bromide, nitric acid was rejected as a means of decomposing marble, and very dilute hydrochloric acid was used instead. The gas was purified by passing through a solution of sodic hydric carbonate, long tubes containing argentic nitrate, and much pure water. Since the last tube containing water gave absolutely no test for chlorine after over 100 litres of the gas had passed through it, one may safely assume that the purification was sufficient. The gas was dried by means of sulphuric acid and phosphoric pentoxide.

(To be continued).

Detection of Nitric Acid in proof of the addition of Water to Wines.—F. Leon.—The processes of fermentation eliminate all traces of nitric acid existing in wines; but if traces still appear the suspicion is justified that, after the wine has been matured, an addition of water has taken place containing an impurity of nitric acid. For the detection, the author distils off the alcohol and re-distils the residue with zinc turnings, so slowly that only about 10 c.c. are obtained in half-an-hour. In this portion nitrous acid is tested for by the process of Griess.—*Gazzetta Chimica and Berichte*.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 7th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Llewellyn John Davies, 8, Wordsworth Avenue, Cardiff; Frederick William Harris, 62, Rectory Road, Burnley; John Burnett Knight, Bushwood, Wanstead, Essex; Percy Sykes Marshall, Church School House, Lockwood, Huddersfield; Loxley Meggitt, The Laurels, St. John's Street, Mansfield; Sigmund Georgjewitsch Rosenblum, 19, Russell Road, Kensington; Douglas Stuart Spens Stewart, 9, Thistle Grove, Fulham Road, S.W.; James Whitehead, Roach Place, Rochdale.

The following were duly elected Fellows of the Society:—Henry Thomas Durant, Ernest Hunter Fisher, W. Goodwin, Edgar Hawkins, John Percival Jenkins, Robert Hazlewood Jones, Herbert Edwin Macadam, John McCrae, jun., William Henry Merrett, Joseph W. Patterson, H. von Pechmann, Thomas William Pilley, Robert Barnabas Pollitt, James Proude, Charles H. Reissmann, Henry Fishwick Robinson, Otto Rosenheim, Raymond St. George Ross, Walter Dalrymple Severn, John Christopher Stead, James Edward Shum Tuckett, Edward Channing Wills, John Henry Wolfenden.

Of the following papers those marked * were read:—

*60. "Carbon Dioxide, its Volumetric Determination." By W. H. SYMONS and F. R. STEPHENS.

After reviewing the various methods for estimating carbon dioxide in air, the authors describe one which they find to be reliable and at the same time convenient.

For collecting the samples of air they use flasks from which all air has been expelled by means of steam, their vacuity being ascertained by weighing before and after use. For absorbing the carbon dioxide, mixed solutions of sodium hydroxide and barium chloride are used. The pressure of the sample of air in the flask is made equal to the atmospheric pressure by admitting a measured volume of air free from carbon dioxide, and the true volume is found by calculation; thus the pressure, and temperature at the time of taking the sample need not be noted. The residual hydroxide is titrated, without being removed from the flask, with dilute acetic acid and phenolphthalein.

The use of the same flask for collecting and cultivating micro-organisms, estimating albumenoid ammonia and oxygen absorbing matter, is suggested, and it is pointed out that the carbon dioxide may be estimated in the same sample of air, provided the number of organisms is not sufficient to influence the results through the carbon dioxide they produce.

Examples of the trustworthy nature of the process are given; in some cases carefully measured volumes of carbon dioxide have been estimated; in others, a series of samples have been taken from a closed space occupied by the authors. A compound pipette for accurately measuring volumes of gas or liquids is also described.

*61. "On certain Views concerning the Condition of the Dissolved Substance in Solutions of Sodium Sulphate." By R. F. D'ARCY, M.A.

The differences in the solubilities of anhydrous sodium sulphate and its two well-defined hydrates, and the existence of a maximum solubility of the decahydrate at a temperature just below that at which it breaks up in the solid state into anhydrous salt and water, are properties which have been thought to indicate that these substances dissolve as such.

Other facts have been shown to be in accordance with the view that the condition of the dissolved salt is the same in all cases—the differences in solubilities being

explained as being determined by the condition of the undissolved solid in contact with the liquid.

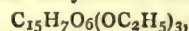
The experiments described were undertaken with the object of finding if any evidence in favour of the former, and now rather discredited, theory could be obtained by making careful experiments on the viscosities of strong solutions of this salt, prepared in different ways and at different temperatures. The results obtained are in accordance with the view of the identity of the condition of the dissolved substance in all cases.

The experimental method, which differs in some respects from those used in other researches, is believed to give results which are free from ambiguity.

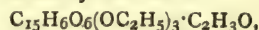
*62. "Luteolin. II." By A. G. PERKIN.

In a previous communication (*Trans.*, 1896, lxi., 206), it was shown that the formula of luteolin is $C_{15}H_{10}O_6$, a fact determined by means of its compounds with mineral acids and with bromine. The production of its tetracetyl and benzoyl compounds proved it to contain four hydroxyl groups, and on methylation it yielded a product containing three methoxy-groups. Since the publication of this paper, Herzig (*Ber.*, xxix, 6, 1013) has stated that he is also working upon luteolin. He mentions the methyl ether of the acetyl compound, and the decomposition of luteolin with fused alkalis. It is now shown that the product previously described, m. p. 210° , which, together with protocathechuic acid is formed by the action of fused alkalis upon luteolin, which did not then appear to be phloroglucol, is really this substance, as surmised by Herzig (*loc. cit.*).

On ethylation, luteolin yields a triethyl ether—



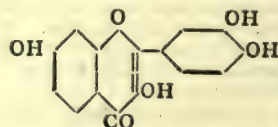
(yellow needles, m. p. $131-132^\circ$), insoluble in alkalis, which gives a monacetyl derivative—



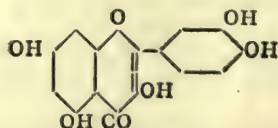
(colourless needles, m. p. $185-186^\circ$). Decomposed by alcoholic potash this ether yields a crystalline yellow potassium salt, which is resolved by water into the free ether. These reactions prove that the hydroxyl group in luteolin which resists ethylation is in the ortho-position to a carbonyl group.

When heated with alcoholic potash to $130-140^\circ$, luteolin triethyl ether yields the diethylether of protocathechuic acid, and a small quantity of a substance which gives the phloroglucol reaction. The product of the methylation of luteolin (*loc. cit.*) closely resembles the ethyl ether in its reaction, as it contains three methoxy-groups, yields an acetyl compound, m. p. $174-175^\circ$, and a yellow potassium salt. Herzig (*loc. cit.*) gives the melting-point of acetyl-luteolin $225-227^\circ$, but an examination of the melting-point previously obtained, $213-215^\circ$, shows that this must be considered as correct.

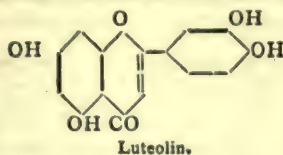
A close resemblance of luteolin to quercetin and fisetin is traced, and it is considered that quercetin, which is an hydroxyfisetin, is most probably also an hydroxyluteolin.



Fisetin.



Quercetin



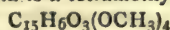
*63. "Morin." Part I. By HERMANN BABLICH, Ph.D., and ARTHUR GEORGE PERKIN.

The yellow colouring matter, morin, exists, as has been known for some time, in old fustic (*Morus tinctoria*), and has lately been shown by one of us and F. Cope (*Trans.*, 1895, 937) to be also contained in the Indian dye-stuff, Jackwood (*Artocarpus integrifolia*). By means of its compounds with mineral acids the true formula of morin was established by one of us and L. Pate (*Trans.*, 1895, lxvii, 644) to be $C_{15}H_{10}O_7$.

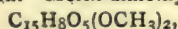
The principal reactions of morin described by previous workers are its behaviour towards alkaline reducing agents (Hlasiwetz and Pfandler, *Fahres.*, 1864, 537), by which means it yields phloroglucol and β -resorcylic acid, and towards fused alkali, when it gives phloroglucol and resorcinol. Of the substitution products of morin but three are described, viz., morinsulphonic acid, $C_{15}H_9O_7HSO_3$ (Benedikt and Hazura, *Monatsh.*, v., 167), tetrabromomorin, $C_{15}H_6Br_4O_7$, and tetrabromomorinethyl ether, $C_{15}H_5Br_4O_7 \cdot C_2H_5$. The latter is formed by brominating morin in alcoholic solution, and can be converted into tetrabromomorin by means of zinc chloride and fuming hydrochloric acid.

The action of fused alkalis and of bromine upon morin has been investigated, and it is shown that by the former means at $150-160^\circ$ phloroglucol and β -resorcylic acid are the principal products, and with the latter the results of Benedikt and Hazura have been confirmed. Incidentally it has been found that, by the action of bromine on morin in presence of acetic acid, a considerably increased yield of tetrabromomorin is obtained.

On acetylation, tetrabromomorin yields pentacetyl-tetrabromomorin, $C_{15}HBr_4O_7(C_2H_3O)_5$ (colourless needles, m. p. $192-193^\circ$), from which it is evident that morin contains five hydroxyl groups. The principal product of the methylation of morin is a tetramethyl ether—



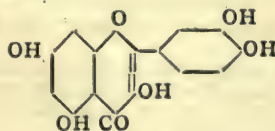
(light yellow needles, m. p. $131-132^\circ$). This substance is insoluble in alkalis, but yields a monacetyl derivative, $C_{15}H_5O_3(OCH_3)_4 \cdot C_2H_3O$ (colourless needles, m. p. 167°), and a crystalline yellow potassium salt, which is decomposed by water, regenerating the ether. When digested with alcoholic potash at $150-160^\circ$, the tetramethyl ether yields the dimethyl ether of β -resorcylic acid (m. p. $107-108^\circ$) and a small quantity of a product which gave the phloroglucol reaction. Morin dimethyl ether—



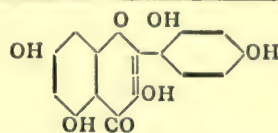
forms yellow needles melting at $255-227^\circ$.

These results demonstrate a close similarity between quercetin and morin, for both contain five hydroxyl groups, one in the ortho-position to a carbonyl group, and both combine with mineral acids. Quercetin yields with fused alkali phloroglucol and protocatechuic acid, morin, phloroglucol, and β -resorcylic acid.

The formula of quercetin appears to be (Herzig, *Ber.*, 1895, xxviii., 223)—



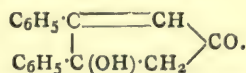
and it seems most probable that the formula of morin is represented by that of quercetin, in which the catechol nucleus has been displaced by a resorcinol group thus—



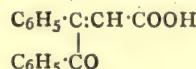
64. "Synthesis of Pentacarbon Rings. Part I. Anhydrazetonebenzil and its Homologues." By FRANCIS R. JAPP, F.R.S., and G. DRUCE LANDER, B.Sc.

Anhydrazetonebenzil, which is obtained by the condensation of benzil with acetone, was first prepared and investigated by Japp and Miller (*Trans.*, 1885, xlvii., 27), and was afterwards further studied by Japp and Burton (*Trans.*, 1887, li., 420). In both of these earlier communications the opinion was expressed that in the condensation a closed chain of carbon atoms was formed.

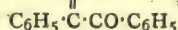
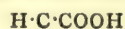
The authors now show that the compound is a diphenyl-hydroxycyclopentenone of the formula—



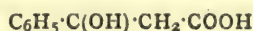
By oxidation with sodium hypobromite it gives an almost quantitative yield of Japp and Davidson's *desylacetic acid*—



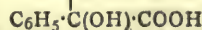
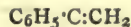
a reaction which constitutes the best means at present known of preparing this compound, and at the same time proves the configuration of the acid to be—



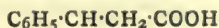
The oxidation of anhydrazetonebenzil by heating it with chromium trioxide in acetic acid solution was studied by Japp and Miller (*loc. cit.*). They thus obtained a product to which they assigned the constitution of a β -benzoyl-hydrocinnamic (desylacetic) acid. Desylacetic acid has, however, been since prepared by Viktor Meyer and Oelkers. The present authors find that the two substances are quite distinct. They also find that Japp and Miller's acid is not the primary product of oxidation, for, when the process is conducted in the cold, simultaneous oxidation and hydration occur, and diphenyldihydroxyglutaric acid—



(m. p. 120° , when rapidly heated), is formed. On heating this acid for some time at 100° it decomposes, parting with carbon dioxide and water, and yielding Japp and Miller's acid, which has the formula of an isocinnamenylmandelic acid—



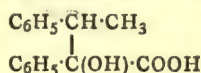
and which melts at $159-160^\circ$. (The melting-point, 152° , given by Japp and Miller is too low). When boiled with fuming hydriodic acid, or with fuming hydrochloric acid, diphenyldihydroxyglutaric acid also parts with carbon dioxide and water; but the carbon dioxide is in this case furnished by the other carboxyl group, and desylacetic acid—



(m. p. 162°), is formed. Beyond the close approximation of the melting-points, there is hardly any resemblance, either physical or chemical, between these two isomerides, desylacetic acid and isocinnamenylmandelic acid.

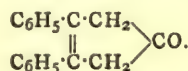
By a partial reduction of isocinnamenylmandelic acid

by boiling it for a few minutes with hydriodic acid, it is converted into *isophenethylmandelic acid*—

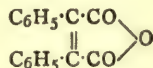


(m. p. 134—136°).

By partial reduction of anhydrazetonebenzil with hydriodic acid, Japp and Burton obtained a compound, $\text{C}_{17}\text{H}_{14}\text{O}$, melting at 110°, which yielded a hydrazone, and therefore contained the original carbonyl group of the anhydrazetonebenzil. The authors show that this reduction compound has the formula of a *diphenylcyclopentenone*,—

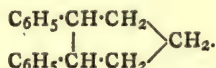


That the foregoing change in the position of the double bonds has taken place during the reduction is shown by the fact that the compound yields, on oxidation with sodium hypobromite, diphenylmaleic acid, which, when liberated from its salts, changes into the very characteristic anhydride,—

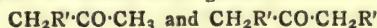


(m. p. 156°).

The hydrocarbon, $\text{C}_{17}\text{H}_{18}$ (m. p. 47°), obtained by Japp and Burton by the complete reduction of anhydrazetonebenzil with hydriodic acid and amorphous phosphorus is a *diphenylcyclopentane*,—



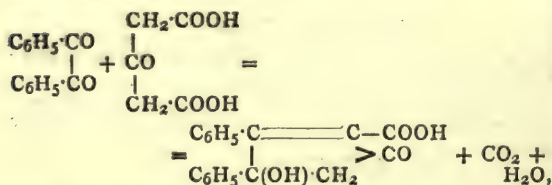
The various compounds obtained by Japp and Burton (*Trans.*, 1887, li., 431) by the condensation of benzil with homologues of acetone of the general formulæ—



must be regarded as homologues of anhydrazetonebenzil.

65. "Synthesis of Pentacarbon Rings. Part II. Condensation of Benzil with Acetonedicarboxylic Acid." By FRANCIS R. JAPP, F.R.S., and G. DRUCE LANDER, B.Sc.

Benzil and acetonedicarboxylic acid, when gently warmed with dilute alcoholic potash, condense according to the equation—



yielding *anhydrazetonebenzilcarboxylic acid* (m. p. 167—168°), which corresponds with isophenanthroxyleneacetacetic acid (Japp and Klingemann, *Trans.*, 1891, lix., 2).

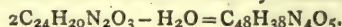
When anhydrazetonebenzilcarboxylic acid is boiled for a few minutes with fuming hydriodic acid, it is reduced, simultaneously parting with carbon dioxide and yielding a *diphenylcyclopentenone* (m. p. 110°), identical with that obtained from anhydrazetonebenzil itself (see preceding note).

By oxidation with sodium hypobromite, anhydrazetonebenzilcarboxylic acid yields a mixture of *diphenylmaleic* and *diphenylfumaric acids*, these two substances being produced in approximately equal quantity. A change in the position of the double bonds takes place during this process.

When oxidised with chromium trioxide in acetic acid solution it parts with 2 atoms of hydrogen, yielding an

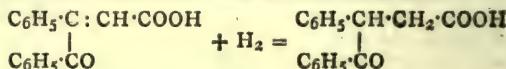
acid of the formula $\text{C}_{18}\text{H}_{22}\text{O}_4$ (m. p. 201°, with decomposition).

The action of phenylhydrazine is complex. The primary product is a yellow compound, apparently the hydrazone; but this readily changes, especially on recrystallisation, into dark red needles of a substance melting indefinitely above 200°, formed by elimination of 1 mol. of water from 2 mols. of the hydrazone,—

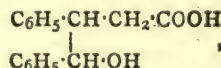


66. "Reduction of Desyleneacetic Acid, and the Constitution of Zinin's Pyroamaric Acid." By FRANCIS R. JAPP, F.R.S., and G. DRUCE LANDER, B.Sc.

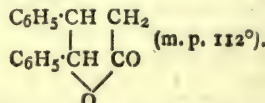
The authors find that by the action of zinc dust and acetic acid on desyleneacetic acid the latter is converted into Victor Meyer and Oelkers's *desylacetic acid*,—



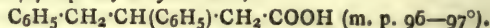
By the limited action of sodium amalgam on an aqueous solution of sodium desyleneacetate the same product is obtained. Excess of sodium amalgam, however, carries the reduction further, and $\beta\gamma$ -diphenyl- γ -hydroxybutyric acid,—



is formed, which, when liberated from its salts, speedily changes into the lactone—



By boiling desyleneacetic acid for four hours with hydriodic acid and amorphous phosphorus, it is converted into $\beta\gamma$ -diphenylbutyric acid,—



Comparison of this substance with a specimen of *pyroamaric acid* showed that the two were identical. Pyroamaric acid was first obtained by Zinin (*Fahresbericht*, 1877, 813) by fusing amaric acid with caustic potash, and was regarded by him as an ethylbenzylbenzoic acid. Klingemann (*Annalen*, cclxxv., 81) suggested that it might be a diphenylbutyric acid.

Incidentally it was observed that when desyleneacetic acid is boiled with aqueous caustic potash it is hydrolysed, yielding deoxybenzoin. Desylenemalonic acid is stable under these conditions.

67. *Electrolysis of Potassium Allo-ethylic Camphorate. Part II.* By JAMES WALKER, Ph.D., D.Sc., and JAMES HENDERSON, B.Sc.

In addition to the compounds previously described (*Trans.*, 1895, 337) the authors have obtained from the product of electrolysis of potassium allo-ethylic camphorate, a hydrocarbon, C_9H_{14} , boiling at 120°, which is formed by the decomposition of an acid, $\text{C}_9\text{H}_{14}\text{O}_2$, on heating. This hydrocarbon is apparently identical with *laurolene* prepared from camphanic acid. A ketonic acid, $\text{C}_9\text{H}_{14}\text{O}_3$, m. p. 228°, was also isolated and investigated. The authors conclude that camphoric acid contains the complex $-\text{CH}_2\cdot\text{CH}(\text{COOH})\cdot\text{C}(\text{COOH})-$.

68. "Fluorene and Acenaphthene." By W. R. HODGKINSON.

Some recent communications in the *Annalen*, by Gräbe and his students, on fluorene and acenaphthene, necessitate a short notice on my part about these substances in order to maintain priority.

The author has worked at these hydrocarbons and their derivatives for the past twelve years, and in *Proc.*, 1885, 36, reference is made to previous notes on the behaviour of fluorene ($\text{C}_{13}\text{H}_{10}$) when heated alone, in air, or with

oxidising agents. Lately he has associated Mr. A. H. Coote with this work.

In the paper above quoted it is indicated that the red substance obtained from fluorene (and also from acenaphthene) can be separated from the hydrocarbons (there called difluoryls, $C_{26}H_{18} \alpha, \beta, \gamma$), and that this red substance is not a simple hydrocarbon, but contains oxygen.

During the past three years a great number of results have been obtained.

One conclusion arrived at is that no red or coloured hydrocarbon is produced by the oxidation of either fluorene or acenaphthene. The coloured compounds produced, along with the doubled molecule in the case of fluorene, $C_{26}H_{18}$ (difluoryl), and the coloured substance along with acenaphthylene in the case of acenaphthene, have been obtained almost pure. It is found that not only on heating with litharge, as Behr and Van Dorp first showed, but that almost any other oxide, and even potash, soda-lime, and chalk Iceland spar, will produce coloured oxidation products from both fluorene and acenaphthene, and especially from the latter. Phenanthrene, naphthalene, and anthracene do not act in the same manner.

On the other hand, both fluorene and acenaphthene may be passed along with hydrogen, steam, or hydrogen chloride, through a red hot platinum tube without change. The isolation of these oxidation products is a difficult matter. They are not volatile alone without decomposition, and are as soluble in the usual liquids as the hydrocarbons. Picric acid also seems to precipitate them as well as the hydrocarbons.

The ethereal and chloroform solutions of these oxidation products are highly fluorescent. The one from acenaphthene more so than that from fluorene. They form compounds with acid sulphites which are non-fluorescent. Two analyses (preps. 5 and 7) taken at random:—

C = 80.41, H = 4.51, O = 15.08.
C = 79.89, H = 4.22, O = 15.89.

The coloured substance from fluorene is more difficult to obtain in quantity, or pure. The average percentage of oxygen is between 9 and 10.

Sulphur behaves like oxygen towards both these hydrocarbons, and selenium also to a lesser extent. When the hydrocarbons are heated with dry sodium thiosulphate, or with some metallic sulphides, sulphur compounds of a red or orange colour are produced. Their solutions in ether and chloroform are also fluorescent. With sulphur or selenium, hydrogen sulphide and selenide are respectively produced. In the case of fluorene a difluoryl is also produced on heating with sulphur.

Several analyses of the red compound from acenaphthene and sulphur indicate the presence of about 13.26 per cent of sulphur.

Research Fund.

A meeting of the Research Fund Committee will be held in June. Applications for grants, accompanied by full particulars, should be sent to the Secretaries before June 8th.

PHYSICAL SOCIETY.

Ordinary Meeting, May 22nd, 1896.

Prof. AYRTON, Vice-President, in the Chair.

MR. R. APPLEYARD read a paper on "Dielectrics."

The author has particularly investigated the effect of temperature on the dielectric resistance. He has employed for this purpose condensers insulated with mica and paraffined paper. In order to eliminate some of the effects of surface leakage, Price's guard-ring arrangement was made use of in all the experiments.

The author finds that the capacity of a paraffin con-

denser varies irregularly with the temperature, but that to within the accuracy attainable with his instruments (1 per cent) the capacity of a mica condenser is constant between 33° F. and 110° F.

If the resistance of paraffin at a temperature t is represented by $R_t = R_a e^{\alpha t}$, the mean value for $\log. \alpha$, deduced from all the author's measurements, is $\bar{r}96344$.

Experiments made with a parallel plate condenser, with paraffin as the dielectric, show that when the temperature reaches within about 20° of the melting-point the resistance rapidly falls; when melting commences there is a rapid drop, but while melting is in progress the resistance remains constant.

Prof. AYRTON said he could bear witness to the extreme value of Mr. Price's device, as it completely did away with the necessity for the extreme care previously required to prevent errors due to surface leakage. He regretted that he had not had an opportunity of comparing the author's numbers with some obtained some years ago by Prof. Perry and himself (Prof. Ayrton).

A paper by Prof. VIRIAMU JONES, on "The Magnetic Field due to an Elliptical Current at a point in the Plane of the Ellipse and within it," was taken as read.

Prof. SILVANUS THOMPSON said that this paper was of interest, not only on account of the application which others might make of the author's method, but also in that the correction, when applied to Prof. Jones's results, brought the international ohm more nearly into accord with the true ohm.

Mr. J. J. WALKER said he considered that the paper was more suited to the Mathematical Society. The integration which the author reduced to elliptic integrals might be more easily performed by another method.

Prof. AYRTON said that Prof. Jones's value for the true ohm was now 106.302 c.m. of mercury.

Mr. CAMPBELL read a paper on "New Instruments for the Direct Measurement of the Frequency of Alternating or Pulsating Electric Currents."

The author employs two arrangements, in one of which a steel wire the tension on which is variable, and the other a steel spring of variable length clamped at one end, are acted upon by an electro-magnet through which the periodic current is passed. The tension or length, as the case may be, is varied till maximum resonance is obtained, a small contact piece being employed to detect when this occurs. The instrument exhibited was capable of measuring the frequency of periodic currents of from 40 to 150 double vibrations per second.

Mr. WATSON said he thought that in the case of the spring there would be a considerable temperature correction, and he suggested a method by which this might be compensated.

Mr. BLAKESLEY asked if the author had found that the spring became magnetised, and thus gave the octave.

Mr. CARTER asked whether elastic fatigue influenced the results, and said that a synchronous motor and a speed indicator could be used to measure the frequency.

Prof. SILVANUS THOMPSON suggested that it might be better to employ a polarised apparatus, since, to avoid the impression of forced vibrations on the spring, it was better, as was done in the case of tuning-forks, to make it massive. It had been found in other cases, such as in Hughes's telegraph and the telephone, that better results were obtained with polarised apparatus. He (Prof. Thompson) had used a telephone, placed anywhere near a magnet traversed by the periodic current, together with a tuning-fork, which gave beats with the note produced by the telephone, to measure frequencies. The variations in frequency ordinarily met with in practice were much greater than was generally suspected.

Mr. BLAKESLEY said he considered that the advantage of the author's instrument over a telephone and tuning-fork was that it was continuously variable over a large range.

Mr. ENRIGHT asked if the author had been troubled by

the spring or wire breaking into overtones. In some experiments, in which rather long wires were used, he had been troubled in this way.

Prof. AYRTON said that he did not think that it was possible to get the wire or spring to respond to the octave unless the alternating current contained a component of the frequency of the octave. In fact, he had himself used such a stretched string as a wave analyser. He had used a telephone to prove that the note given by a hissing alternate current arc corresponded in frequency to that of the current. In the instrument used by Prof. Perry and himself a polarised arrangement was always employed, since the alternating current was passed either through a wire in a constant magnetic field, or through an electromagnet which acted on a wire through which a constant current was passed.

The Author, in his reply, said that the instrument responded, though feebly, to the octave, and this response might be made use of to check the accuracy of the scale.

The Society then adjourned till June 12th.

NOTICES OF BOOKS.

Synopsis of Current Electrical Literature: compiled from [fifty-nine American and Foreign] Technical Journals and Magazines during 1895. By MAX OSTERBERG. *Electric Power*, 27, Thames Street, New York; D. van Nostrand Co., 23, Murray Street, New York. 1896. Pp. xiii.—143, 8vo.

WHILE the Royal Society is making plans for indexing scientific literature of the next century on a grand scale, the Office International de Bibliographie, at Brussels, is stimulating the efforts of the French-speaking people, and the Bureau of Zoological Literature established by Dr. Field at Zurich is furnishing a centre of influence for the whole world of zoologists, the Americans are pushing forward in the same lines. The bibliographical publications of the Smithsonian Institution are well known and highly valued; the superb Index-Catalogue of the Medical Library of the U.S. Army, successfully concluded last year by its distinguished director, Dr. John S. Billings, furnishes the highest model of excellence to all librarians; the labours of the Committee on Indexing Chemical Literature of the American Association for the Advancement of Science, now in its fourteenth year of activity, are well known through its reports annually published in the *CHEMICAL NEWS*. Besides these concerted efforts, individual enterprise in America is accomplishing much good work of a kindred nature: of such is the volume now under review. Mr. Osterberg's *Monthly Journal, Electric Power*, offers its readers *Synopses of current electrical literature*, and this material re-arranged in convenient form constitutes this annual volume.

The compiler states that the principal aim has been to give the "headings and names of authors of the most important articles pertaining to electricity published in the English, German, and French languages during the past year." This has certainly been accomplished; the titles are followed by brief comments characterising the article cited. The titles are grouped under the sixteen following heads:—

Alternating Currents; Biographical; Central Stations; Dynamos and Motors; Educational; Electro-chemistry; Electro-physics; Electro-therapeutics; Isolated Plants; Lighting (Arcs, &c.); Magnetism; Measurements and Instruments for Measuring; Railways; Storage Batteries; Telegraphy, Telephony, &c.; Transmission and Power.

There is an author index. The book will prove invaluable to every electrician who desires to keep abreast of the times.

Handbook for the Biochemical Laboratory, including Methods of Preparation and numerous Tests, arranged Alphabetically. By JOHN A. MANDEL, Professor of Chemistry at the New York College of Veterinary Surgeons, and Assistant to the Chair of Chemistry at the Belle Vue Hospital Medical College and the College of the City of New York. First Edition. First Thousand. New York: J. Wiley and Sons. London: Chapman and Hall, Ltd. 1896.

THE American press is at present fairly fruitful in chemical publications, and not so much in sketchy pamphlets and "manualettes," written in accordance with the latest syllabus, one of them differing from another barely enough to satisfy the law of copyright as in sound publications. The work before us will be unquestionably useful to the chemical student, to the praktikan,—an English word is here wanting,—and to the physician. We find here, firstly, directions for preparing in a state of purity the most important fluids and tissues which enter into the composition of the animal body.

Then follow tests for the animal constituents, in number exceeding two hundred. We must of course admit, if that be any fault, that there is here no little which will grind the gentle spirit of Victoria Street

"Into a powdery foam of salt abuse,
Ruffling the ocean of their self content."

But none the less do we wish Mr. Mandel's work good speed and a large circulation.

Handbook of Chemical Technology. ("Handbuch der Chemischen Technologie"). Elaborated in association with several Savants and Technicians. Edited by Dr. P. A. BOLLEY and Dr. K. BIRNBAUM. Continued, after the death of the Editors, by Dr. C. ENGLER, Privy Aulic Councillor and Professor of Chemistry at the Technical High School of Carlsruhe. Eight Volumes, mostly divided into several groups. First Volume—Third Group: Chemical Technology of Fuel. By Prof. Dr. FERDINAND FISCHER, of Göttingen. With numerous Woodcuts in the Text. London, Edinburgh, and Oxford: Williams and Norgate. 1896.

AFTER a brief section on the liberation of heat in and by chemical action, the author passes in review the principal kinds of fuel. As regards wood, we learn that amongst the European countries, England—probably Britain—has the lowest percentage of land occupied by woods, namely 4.0, whilst Denmark has 4.8 and Portugal 5.3. This circumstance we may remark is due to local taxation.

In some kinds of timber the proportion of moisture reaches, or even exceeds, 50 per cent. The proportion of ash in heart-wood is highest in the horse-chestnut, 2.8 per cent; in the oak and the beech, 0.5, and in the firs as low as 0.21. Under some circumstances more phosphorus may be introduced into iron during smelting with charcoal than with coke. The average amount of phosphorus in the beech charcoal is 0.1485 per cent, and in coke from Ostrau only 0.024 to 0.052.

Peat or turf has been in use as a domestic source of heat from the time of Pliny. The chief agents in its formation are the heaths *Calluna vulgaris* and *Erica tetralix*, the mosses, such as *Sphagnum* and *Hyphnum* (species), and a variety of other plants, the separate functions of which in the formation of peat is not completely understood. The utilisation of heat by pressing and exsiccation has been the subject of many inventions, none of which seem to have given complete satisfaction. Hence the use of peat is chiefly confined to localities where coal and wood are not easily procurable. Certain peats—i.e., those of Berks, Hants, &c.—have a destructive influence upon vegetation due to the presence of ferrous sulphide and possibly arsenide (?).

Coal has now for a long time taken the lead among fuels, at least for industrial purposes. Its use may be

traced back to a high antiquity. According to Lyell, coal must have been used in Scotland some 5000 years ago. There is evidence that the Romans made use of coal at their settlements in England. Pliny and Vitruvius, remarkably enough, make no mention of this fact. Coal-mining at Zwickau can be traced back to the tenth century, and by the year 1348 their combustion was found to be a nuisance. Coal-smoke was even said to have occasioned the plague! Legislation against coal-smoke was initiated in England in the reign of Edward I., but proved a complete failure, as did the subsequent enactments of Queen Elizabeth.

The coal-deposits of China are, on the authority of Von Richthofen, estimated as the most important of the entire globe. The coal-beds of Natal and the adjoining parts of the Orange Free State have been overlooked in this survey, though they are reputed as being more valuable than those of Britain, even before they had begun to be worked.

The warning is given that the earth's supply of coal, though vast, is by no means inexhaustible, and that with its end the present culture of Europe must cease. Hence the existing stores should be used judiciously.

The ash of coal often contains phosphoric acid, according to Le Chatelier, in quantities up to 3 per cent. The ash of Westphalian coal, according to Platz, contains as much as 0.5 per cent of copper, lead, and zinc. Arsenic is also not absent, appearing in the form of arsenical pyrites. Coal and soot contain from 0.89 to 0.117 per cent of arsenious acid. Nickel, thallium, and lithium are also occasionally present. Some coals contain barium sulphate.

The subject of explosions in coal-mines and coal-magazines is very fully discussed. The loss of life in the chief States of Europe from 1871 to 1880 is given at no fewer than 4471 men, more than the half of this loss—2686 men—being the share of Britain. But the coal industry in the same decennium and in the same countries cost altogether the lives of 21,256 men, King Coal having demanded the sacrifice of 16,785 lives in other manners. It is here rightly held that, in spite of the best ventilation, the use of good safety lamps and suitable blasting materials is of the utmost importance. The authors seem scarcely to ascribe sufficient importance to the part played in the explosions by coal-dust.

Nearly connected with this subject is the so-called spontaneous ignition of coal on ship-board, in magazines, &c. The majority of experts think now that ventilation is no safe remedy. Of 70 coal-ships lost by spontaneous combustion in 1874, it is certain that 38 were ventilated, whilst the contrary is not reported of any of the rest. Smalls and moist lots are generally condemned, as is also highly pyritiferous coal, especially if the pyrites is present not in lumps, but in minute quantities.

A proposal of the highest value—if not too expensive—is to place, among the coal in the hold, bottles containing compressed carbon dioxide, and closed with stoppers fusible at certain temperatures.

It is generally recognised that the danger of spontaneous ignition on board ship increases with the quantity of coal. A vessel carrying 500 tons of coal is rarely in peril of fire, whilst cargoes of 1500 to 2000 tons have often been destroyed by fire. It is recommended that coal should not be shipped very fresh from the mine.

Action of Hydrobromic Gas upon Thiophosphoryl Chloride.—A. Besson.—The compound resulting, PSCl_2Br , distils at 80° under a reduced pressure. Under the action of cold it becomes a white solid body fusible at -30° . At 0° its sp. gr. = 2.12. In contact with cold water it is slowly decomposed, but more quickly by an alkaline or ammoniacal solution, with liberation of sulphur. In contact with fuming nitric acid there is a violent reaction, which is much less violent with acid at 36° , when the sulphur and phosphorus are converted into sulphuric and phosphoric acids.—*Comptes Rendus*, cxvii., No. 19.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvii., No. 18, May 4, 1896.

Electrostatic Deflection of the Kathodic Rays.—G. Jaumann.—(In reply to H. Poincaré).—These feeble rays are very strongly deflected by electrostatic rays. A rod of glass rubbed and agitated at the distance of 50 c.m. from the tube deflects the rays. A rod of ebonite deflects them in a contrary direction. Charged conductors deflect them in corresponding directions.

Apparatus for the Measurement of Currents of High Frequency.—G. Gaiße and E. Meylan.—The author discusses the thermic galvanometer and the induction ammeter.

Reply to the Observations of Auguste Righi.—L. Benoist and D. Hurmuzescu.—The authors consider that it results from their experiments, as well as from those of Righi, that the action of the X rays upon an electrified body is the total dissipation of its electricity, as if the conductor were in connection with the earth. Now, in cases where there exist electromotive contact forces, the conduction to earth causes exactly the existence of an electrification of the magnitude of one volt.

Relation between the Maximum Production of X Rays, the Degree of the Vacuum, and the Form of the Tubes.—Vidtor Chabaud and D. Hurmuzescu.—This paper cannot be inserted without the accompanying woodcuts.

Radiographs. Applications to the Physiology of Movement.—A. Imbert and H. Bertin-Sans.—After the radiographs of the wrist, the elbow, and the knee, which we have had the honour of submitting to the Academy, we have obtained analogous results for the shoulder, the tarsus, and the lumbar region of the vertebral column. All these proofs have been obtained from the living subject.

Transformation of Tariric Acid and of Stearoleic Acid into Stearic Acid.—A. Arnaud.—The tariric acid which the author discovered some years ago in the seeds of the Tarin of Gautemala (*Picramnia*, sp. x of the *Simarubiacæ*) is a crystalline fatty acid belonging to the non-saturated crystalline series, $\text{C}_{27}\text{H}_{48}\text{O}_2$. It is isomeric with stearoleic acid. Tariric acid belongs to the oleic-stearic group.

Presence in *Monotropa hypopithys* of a Glucoside of the Methylsalicylic Ether, and on the Hydrolysing Ferment of this Glucoside.—Em. Bourquelot.—It results from all the facts adduced that one and the same hydrolysing ferment of gaultheria exists in the roots of *Spirea ulmaria*, *filipendula*, and *salicifolia*; in the root of *Polygala*; in the bark of *Betula lenta*; in the leaves and the fruits of *Gaultheria procumbens*; and in the petals of *Asalea*. There exists in *Monotropa hypopithys* a glucoside which is hydrolysed by this ferment, and which is in consequence probably identical with gaultherine. This ferment is probably peculiar, for neither gaultherine nor the glucoside of *Monotropa* are hydrolysed by this ferment, and the ferment which acts upon these glucosides has no action upon others.

Maize.—M. Ballard.—Maize contains as much nitrogen and phosphatic ash as the average of French wheats, and three or four times more fatty matter. Hence it is a more complete food than wheat.

Fermentation of Uric Acid by Micro-organisms.—E. Gérard.—Uric acid is decomposed by the action of micro-organisms into urea and ammonium carbonate. It

is very probable that the urea, the principal product formed, is subsequently subject to the action of an uruphagous microbe when it is hydrated, yielding ammonium carbonate.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. i., No. 1.

Report by P. Bérard on two Respiratory Appliances by Drs. Detourbe and Détröye.—The Committee of Chemical Arts has awarded a premium to the mask constructed by Dr. Détröye, but at the same time they render full justice to the apparatus presented by M. Detourbe. These respirators cannot be described without the accompanying figure.

The Industrial Work of Pasteur.—E. Duclaux.—The writer gives an account of Pasteur's successful attempt to conquer the silk-worm disease and his studies on fermentation. Incidentally, reference is made to the grand principle of attenuation, by means of which the extirpation of various diseases of mankind are in course of being overcome. By a curious coincidence the paper was read on the anniversary of Pasteur's birthday.

Improvements in the Manufacture of Hydrochloric Acid and of Bleaching Products.—M. Buisine.—The author gives an especial account of the ammonia-soda process, which he considers as at present predominant, though the electrolytic procedures are attracting much attention.

Among the "Chemical Notes" is mention of a case of so-called spontaneous combustion in certain red leads which have been brightened with eosine.

No. 2, 1896.

This number contains no chemical matter.

MEETINGS FOR THE WEEK.

- MONDAY, June 1st.**—Society of Chemical Industry, 8. "Japanese Metallurgy—Part I. Gold and Silver and their Alloys," by W. Gowland, F.I.C. "Electrodeposition of Zinc," by Sherard Cowper-Coles.
- TUESDAY, 2nd.**—Royal Institution, 3. "The Building and Sculpture of Western Europe," by Prof. T. G. Bonney, F.R.S.
Institute of Civil Engineers, 8. (Anniversary).
- WEDNESDAY, 3rd.**—Royal Institution, 3. "Vault of the Sixtine Chapel," by Prof. W. B. Richmond, R.A.
Society of Public Analysts, 8.
- THURSDAY, 4th.**—Royal, 4.30.
Royal Institution, 3. "Lake Dwellings," by R. Munro, M.D., M.A.
Chemical, 8. "The Magnetic Rotation of Organic Substances, with especial reference to Benzenoid Compounds," by Dr. W. H. Perkin, F.R.S.
- FRIDAY, 5th.**—Royal Institution, 9. "Electric and Magnetic Research at Low Temperatures," by Prof. J. A. Fleming.
Geologists' Association, 8.
Quekett Club, 8.
- SATURDAY, 6th.**—Royal Institution, 3. "The Moral and Religious Literature of Ancient Egypt," by Dr. E. A. Wallis Budge, M.A.

THE X-RAYS.

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CITY AND GUILDS OF LONDON INSTITUTE.

SESSION 1896-97.

The Courses of Instruction in ENGINEERING and CHEMISTRY at the Institute's Colleges commence in October, and cover a period of two to three years. The MATRICULATION EXAMINATION of the CENTRAL TECHNICAL COLLEGE will be held on September 21st to 24th, and the ENTRANCE EXAMINATION of the Day Department of the TECHNICAL COLLEGE, FINSBURY, on September 22nd.

CITY AND GUILDS CENTRAL TECHNICAL COLLEGE

(Exhibition Road, S.W.), a College for higher Technical Instruction for students not under 16 years of age preparing to become Civil, Mechanical, or Electrical Engineers. Chemical and other Manufacturers, and Teachers.

THE MATRICULATION EXAMINATION will be held on September 21st to 24th, and the new Session will commence on October 1st.

Professors:—O. HENRICI, LL.D., F.R.S. (Mathematics), W. C. UNWIN, F.R.S., M.I.C.E. (Civil and Mechanical Engineering), W. E. AYRTON, F.R.S. (Physics and Electrical Engineering), H. E. ARMSTRONG, Ph.D., F.R.S. (Chemistry).

CITY AND GUILDS TECHNICAL COLLEGE, Finsbury (Leonard Street, City Road, E.C.). The DAY DEPARTMENT provides Courses of Intermediate Instruction for Students not under 14 years of age, preparing to enter Mechanical or Electrical Engineering and Chemical Industries.

THE ENTRANCE EXAMINATION will be held on September 22nd, and the new Session will commence on October 6th.

Professors:—S. P. THOMPSON, D.Sc., F.R.S. (Electrical Engineering), J. PERRY, D.Sc., F.R.S. (Mechanical Engineering), R. MELDOLA, F.R.S. (Chemistry).

JOHN WATNEY,
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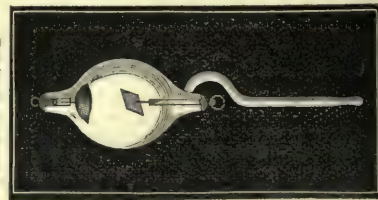
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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1906.

HELIUM AND ARGON.

PART III.—EXPERIMENTS WHICH HAVE YIELDED NEGATIVE RESULTS.*

By WILLIAM RAMSAY, Ph.D., F.R.S., and J. NORMAN
COLLIE, Ph.D., F.R.S.E.

To chronicle a list of failures is not an agreeable task; and yet it is sometimes necessary, in order that the record of the behaviour of newly-discovered substances may be a complete one. It is with this object that we place on record an account of a number of experiments made to test the possibility of forming compounds of helium and argon.

It will be remembered that, in our memoir on Argon (*Phil. Trans.*, vol. clxxxvi., A), Lord Rayleigh and Prof. Ramsay described numerous experiments, made in the hope of inducing argon to combine, all of which yielded negative results. Two further experiments have been since made—again without success.

1. The electric arc was maintained for several hours in an atmosphere of argon. The electrodes were thin pencils of gas carbon, and, previous to the introduction of the argon, the arc was made in a vacuum, and all gas evolved was removed by pumping. Argon was then admitted up to a known pressure, and the arc was again made. A slow expansion took place; one of the electrodes diminished in length, and the bulb became coated with a black deposit. The resulting gas was treated with caustic soda and with a solution of ammoniacal cuprous chloride, and, on transference to a vacuum-tube, it showed the spectrum of argon along with a spectrum resembling that of hydrocarbons. Having to leave off work at this stage, a short note was sent to the *CHEMICAL NEWS* on a "Possible Compound of Argon." On resuming work after the holidays, the gas was again investigated, and, on sparking with oxygen, carbon dioxide was produced. But it was thought right again to treat the gas with cuprous chloride in presence of ammonia, and it now appeared that, when left for a sufficient time in contact with a strong solution, considerable contraction took place, carbonic oxide being removed. There can, therefore, be no doubt that, although apparently all gas had been removed from the carbon electrodes before admitting argon, some carbon dioxide must have been still occluded, probably in the upper part of the electrodes, and that the prolonged heating due to the arc had expelled this gas and converted it into monoxide. It was, indeed, inexplicable how an expansion should have taken place unless by some such means; for the combination of a monatomic gas must necessarily be accompanied by contraction. It appears, therefore, certain that argon and carbon do not combine, even at the high temperature of the arc, where any product would have a chance of escaping decomposition by removing itself from the source of heat. It is hardly necessary to point out that such a process lends itself to the formation of endothermic compounds such as acetylene, and it was to be supposed that, if argon is capable of combination at all, the resulting compound must be produced by an endothermic reaction.

2. A product rich in barium cyanide was made by the action of producer gas on a mixture of barium carbonate and carbon at the intense temperature of the arc. This product was treated by Dumas's process so as to recover all nitrogen; and, as argon might also have entered into combination, the nitrogen was absorbed by sparking. All

the nitrogen entered into combination with oxygen and soda, leaving no residue. Hence it may be concluded that no argon enters into combination. For the successful carrying out of these experiments we have to thank Mr. G. W. MacDonald.

3. A mixture of argon with the vapour of carbon tetrachloride was exposed for several hours to a silent discharge from a very powerful induction coil. The apparatus was connected with a gauge which registered the pressure of the vapour of the tetrachloride and of the argon of which it was mixed. Careful measurement of the pressure was made before commencing the experiment and after its completion. Although a considerable amount of other chlorides of carbon was produced, no alteration of pressure was noticeable, the liberated chlorine having been absorbed by the mercury present. Here again the argon did not enter into the reaction, but it was recovered without loss of volume.

The remaining experiments relate to attempts to produce compounds of helium. The plan of operation was to circulate helium over the reagent at a bright red heat, and to observe whether any alteration in volume occurred—an absorption of a few c.c. could have been observed—or whether any marked change was produced in the reagent employed. As a rule, after the reagent had been allowed to cool in the gas, all helium was removed with the pump, and the reagent was again heated to redness, so as, if a compound had been formed, to decompose it and expel the helium. Every experiment gave negative results; in no case was there any reason to suspect that helium had entered into combination.

A short catalogue of the substances tried may be given.

4. Sodium distilled in the current of gas, and condensed in drops with bright metallic lustre. The glass tube in which it was heated became covered with a coating of—

5. Silicon, which caused no absorption.

6. A mixture of beryllium oxide and magnesium, yielding metallic beryllium, was without action.

7. Zinc, and 8, cadmium, distilled over in the current of gas.

9. A mixture of boron oxide and magnesium dust, giving elemental boron, produced no absorption.

10. Similarly, a mixture of yttrium oxide and magnesium dust had no effect.

11. Thallium was heated to bright redness in the gas, retaining its metallic lustre.

12. Titanium oxide mixed with magnesium dust was heated to bright redness, and caused no absorption.

13. Similar absence of action was proved with thorium oxide and magnesium powder.

14. Tin, and 15, lead, were heated to bright redness in the current of gas, and remained untarnished.

16. Phosphorus was distilled in the gas, and caused to pass through a length of combustion-tube heated to softening. Some red phosphorus was formed, but no alteration of volume was noticed.

17. The same process was repeated with elemental arsenic.

18. Antimony, and 19, bismuth, at a bright red heat, retained their metallic lustre.

20. Sulphur, and 21, selenium, were treated in the same way as phosphorus; no action took place.

22. Uranium oxide, mixed with magnesium dust, was heated to bright redness in helium. No change, except the reduction of the oxide, took place. The mixture was allowed to cool slowly in the current, and the helium was removed with the pump till a phosphorescent vacuum was produced in a vacuum tube communicating with the circuit. The mixture was re-heated, and no helium was evolved—not even enough to show a spectrum. The vacuum remained unimpaired.

It had been hoped that elements with high atomic weight, such as thallium, lead, bismuth, thorium, and uranium, might have effected combination, but the hope was vain.

* A Paper read before the Royal Society, May 21, 1896.

23. A mixture of helium with its own volume of chlorine was exposed to a silent discharge for several hours. The chlorine was contained in a reservoir, sealed on to the little apparatus which had the form of an ozone apparatus. No change in level of the sulphuric acid confining the chlorine was detected after the temperature, raised by the discharge, had again become the same as that of the room. Hence helium and chlorine do not combine.

24. Metallic cobalt in powder does not absorb helium at a red heat.

25. Platinum black does not occlude it.

26. It is not caused to combine by passage over a mixture of soda-lime and potassium nitrate heated to bright redness. This was hardly to be expected, for it resists the action of oxygen in presence of caustic soda, even when heated by the sparks which traverse it.

27. A mixture of soda-lime and sulphur consisting of polysulphides causes no change of volume in a current of helium passed over it at a bright red heat.

28. Induction sparks in an ozone apparatus passed through a mixture of helium with benzene vapour in presence of liquid benzene for many hours, gave no change of volume. The benzene was, of course, altered, but the sum of the pressures of the helium and the benzene vapour remained as at first. Had helium been removed, contraction would have occurred.

This ends the catalogue of negative experiments. Any compound of helium capable of existence will probably be endothermic, and the two methods of producing endothermic compounds, where no simultaneous exothermic reaction is possible, are exposure to a high temperature, at which endothermic compounds show greater stability, and the influence of the silent electric discharge. These methods have been tried, so far in vain. There is, therefore, every reason to believe that the elements, helium and argon, are non-valent, that is, are incapable of forming compounds.

ON THE COLOUR RELATIONS OF ATOMS, IONS, AND MOLECULES.

PART II.

By M. CAREY LEA.

I.—Interaction of Ions.

If a coloured substance be formed by the union of a colourless kation with a colourless anion, the colour belongs to the molecule only. The colourless ions have so modified each others' vibration periods that selective absorption is exercised. As soon, therefore, as the molecule is divided into ions the colour must disappear. Consequently, if we find a solvent which, like water, is capable of separating the ions, the resulting solution, when dilute, must be colourless, no matter how intense the colour of the compound.

The truth of this law of interaction has been tested experimentally in a considerable number of cases. The results, which were found to be without exception confirmatory, are given below.

Alkaline Metals.—These form comparatively few coloured products, soluble in water, by uniting with colourless atoms. Well marked instances are, however, found in the monosulphides.

Potassium sulphide, K_2S , is in the solid form cinnabar-red. It dissolves in water to a colourless solution.* The sodium salt acts similarly. As to the alkaline selenides and tellurides, their tendency to form poly-salts is so great that it is not possible to judge of the colour shown by mono-salts in solution. It is of interest, however, that

hydrogen selenide, and probably, also, the tellurides, are colourless; also, the oxygen acids of both are colourless. There is little doubt, therefore, that selenium and tellurium, like sulphur, have colourless ions.

Mercuric iodide affords an excellent illustration of the principle stated, owing to the large variety of solvents for it.

In hot ethylic alcohol it dissolves easily. Solution absolutely colourless; gives a cloud when poured into water, which settles to a red powder.

Methylic alcohol acts similarly.

In solution of calcium chloride, especially if hot, dissolves easily; less easily in barium chloride.

In solution of potassium and sodium chlorides, dissolves sparingly. All these solutions are colourless.

In solutions of potassium bromide, and of iodide, it dissolves abundantly. Strong solutions have a yellowish colour, but become colourless by moderate dilution. These two salt solutions dissolve mercuric iodide freely in the cold; the other solvents need heat.

In cold solution of mercuric nitrate, it dissolves easily to a colourless solution. In solution of mercuric chloride it is somewhat soluble; the solution is colourless.

In glycerin it dissolves pretty well with the aid of heat, and does not communicate a trace of colour.

Mercuric arsenite is bluish grey. It is slightly soluble in solution of sodium-arsenite. The solution is colourless.

Mercuric arsenate is pale yellow. It dissolves in a solution of mercuric nitrate, and also in one of sodium pyrophosphate; both solutions are colourless.

The black heavy metallic sulphides are very difficult substances to bring into solution, but it seems that when this can be done the solution is colourless when the ions are colourless. This can be shown to be the case with mercuric sulphide and with antimonie sulphide. According to Weber (*cf.* "Gmelin-Kraut," iv., p. 851), when mercuric chloride is precipitated with an excess of ammonium sulphide, the precipitate dissolves in potash to a colourless solution.

Silver oxide is slightly soluble in water. Being very deeply coloured, it would seem natural that its solution should show this colour; but the solution is absolutely colourless. This is because the silver ion is colourless. Metallic oxides having coloured ions carry that colour into their solutions, as is seen in the case of cupric oxide in alkaline solutions, and in soluble forms of ferric oxide.

Silver arsenite is lemon-yellow; it is abundantly soluble in ammonia-water and in mercuric nitrate. Both solutions are colourless.

Silver Arsenate.—Chocolate colour; dissolves in the same solvents as the last, and also gives colourless solutions.

Silver Phosphate.—Triargentic phosphate dissolves with facility in nitric acid, in ammonia-water, and in mercuric nitrate. All three solutions are colourless.

Cuprous Sulphite (Gmelin, "Handbook," Ger. ed. iv., p. 622).—Red; dissolves in ammonia-water and in dilute hydrochloric acid, giving colourless solutions.

Stannic Sulphide, precipitated.—Ochre-yellow; dissolves in warm potash or soda solution; the resulting solution is nearly colourless.

It also dissolves in potassium sulpharsenite to a colourless solution.

Red antimony pentasulphide dissolves in alkaline monosulphides; solutions colourless.

Orpiment (As_2S_3) dissolves easily in warm potash or soda solution; colourless.

2.—Combinations of Ions.

Ions may combine:—A. Two or more similar colourless ions may unite to form a coloured elementary molecule.

The ions of iodine and bromine are colourless, as shown in solutions of HBr and KBr , HI and KI . The molecules are strongly coloured. The ions of lead are colourless, as shown in solutions of lead nitrate or acetate.

* Graham Otto, 5th Ger. ed., vol. iii., p. 240. The reactions here described have been either found or verified by the writer, except in a few instances, and in these, as in the present case, the authority on which they are stated is given.

The molecule (or the polymer) of lead is blue. The ion of sulphur is colourless—water is not coloured when saturated with sulphydric acid. The oxygen acids of sulphur are colourless; but the molecule is yellow. Selenium has a colourless ion, but a strongly coloured molecule. Colourless cuprous ions unite to form red copper.

B. Two or more similar ions, coloured, may unite to form a colourless (or white) molecule, or polymer. The ion of platinum is yellow in Ptiv, red in Ptii; in each case the ions unite to form white platinum. The nickel ion is green; these unite to form white metallic nickel.

C. Two or more similar ions, coloured, may unite to form a molecule of a wholly different colour. Blue copper ions may unite to form red copper.

D. Two or more dissimilar colourless ions may unite to form a coloured molecule. Sulphur and nitrogen unite to form orange-coloured nitrogen sulphide. Sulphur and silver to form black silver sulphide.

It is an interesting fact, and one I believe that has not been previously noticed, that no ion, and therefore no atom, is black, but is always transparent to some portion or portions of the visible rays. In this respect atoms and ions differ absolutely from molecules. For these last are often black, and this may be the case even with elements—as, for example, iodine in the solid form, platinum black, &c. The absolute difference between atoms and molecules, the entire absence of colour relation between them, was mentioned in the first part of this paper; it must always be one of the most remarkable facts in chemistry.

The production of a black molecule in no way depends upon the combination of two or more atoms having different relations to light, such that one should extinguish the rays which the other or others allow to pass. This might almost be expected, but is far from being the case. Two colourless atoms may unite to form a black molecule, as in the cases just mentioned.

It seems scarcely necessary to say that these remarks relate to inorganic molecules only. For in organic molecules, chemical composition has little influence; isomeric combinations exhibit the greatest differences, and their spectra show little relation to those of their elements (Ostwald, "Lehrb.," 2nd Ger. ed., i., 472).

With organic compounds, which are formed almost exclusively of colourless atoms, it is always the colour of the molecule that is important. With inorganic compounds the reverse is the case—we have much less to learn from the colour of the molecule; that of the atom is all important. One and the same molecule may present various colours, absolutely unlike each other. Phosphorus and sulphur may be black, red, or yellow. Gold is yellow by reflected, blue or green by transmitted light, and may be red when in a state of fine division. Who shall say in either case which of these colours is characteristic? With the ion, and therefore with the atom, there is no such ambiguity. Its colour, its absorption-spectrum, are invariable; these are always highly characteristic.

3.—Acid Indicators: Theory of their Reactions.

Acid indicators are such as show a striking change by the addition of an alkaline solution; either from one colour to another, or from a colourless to a strongly coloured solution. They may be considered as of the nature of weak acids. Their reactions have been explained (Ostwald, "Lehrbuch," 2nd Ger. ed., i., 800) in this way: that the radicle has, as an ion, a colour different from that which it has in the undissociated compound.

This explanation is unsatisfactory, for two reasons:—

1. It makes the colour of an acid indicator, in presence of an alkali, depend on dissociation. But it can be shown that such a coloured solution may be evaporated to dryness and thoroughly desiccated at 100° without losing anything of the intensity of its colour; that is, the

colour persists under conditions in which dissociation is impossible.

2. It makes the colour—or absence of colour, as the case may be—of the solution of the acid indicator, when isolated, depend upon the absence of dissociation. But it is a familiar fact that, by sufficient dilution, even the weakest acids are largely or even completely dissociated. (All their molecules become active: Ostwald, "Lehrb.," 2nd Ger. ed., ii., 653; Nernst, "The Ch.," 440).

Let us take litmus for example. This is a weak acid red dye-stuff, which in contact with an alkali becomes blue. According to the explanation here criticised, isolated red litmus has a blue ion, which does not appear in solution because not dissociated. But it is certain that, with sufficient dilution, it must be dissociated; and, according to this explanation, it should then turn blue. Whereas, red litmus remains red by any amount of dilution, so long as any trace of colour is left.

Again, it is said that blue litmus owes its blue colour to dissociation. But the blue solution may be evaporated and desiccated at 100° without losing its blue colour. The colour is, therefore, *not due to dissociation*.

With these complex and faintly acid organic substances it seems probable that some change in their constitution takes place in the presence of an alkali; such that the anion that separates from the dilute solution of the isolated substance is not the same as that which separates from the alkaline combination; that is to say, the anion which separates from red litmus is not absolutely the same as that which separates from blue. Only in this way can the various reactions of acid indicators be satisfactorily explained.

The reactions of these substances have not been studied with sufficient accuracy to indicate exactly what is the change that takes place in the presence of an alkali. It may be either a re-arrangement of some of the atoms, or it may depend on the taking up of one or more molecules of water.

When an alcoholic solution of phenolphthalein is dropped into much water, the resulting solution cannot be distinguished from pure water by its colour. The addition of a trace of potash brings it to a deep rose red. Phenolphthalein acts as a very weak acid; its very dilute solution must therefore be dissociated, and the colourless anion of the isolated substance must differ from the coloured anion which separates from the potash compound.

Also, a solution of the potash compound, so dilute as to leave a transparent film, has been evaporated and then desiccated for many hours at 100°, the colour of the solution still fully remaining in the dry product. Now, the potash compound of phenolphthalein is known to be anhydrous. Anhydrous substances thoroughly desiccated cannot be in a dissociated state, and therefore the rose-red colour of the potash compound is not due to dissociation.

Further, if to the potash solution a solution of a silver salt is added, there is formed a silver compound having the same constitution as that of the potassium compound. This silver compound is anhydrous and insoluble; nevertheless, it has the same colour as the potassium compound under conditions which make dissociation to be out of the question.

Paranitrophenol.—This is another acid indicator. In a solid state it is nearly colourless; it dissolves in warm water to a nearly colourless solution, which, on the addition of an alkali, becomes gold-yellow. A portion of this solution, evaporated so as to leave a thin film, exhibits the same intensity of colour as the solution, which colour it retains after thorough desiccation. The colour of the solution is therefore not due to dissociation. The solution of the substance itself, when largely diluted, gives no indication of the dissociation of a coloured ion. The behaviour of phenacetoline, another acid indicator, is analogous.

It seems, therefore, that dissociation has no essential connection with the reactions of acid indicators. It is

simply that these substances, by combining with alkalis, either have their colour much intensified, or in some cases change it altogether.

Such changes are not in any way confined to acid indicators, so-called. Picric acid, in combining with alkalis, has its colour much intensified; the acid itself has a pale yellow colour; the sodium salt (dry) has a pure deep yellow colour. Chrysammic acid affords an example of a complete change of colour; the acid itself is yellow, the potash salt a deep blood red, not only in solution, but in the dry state, so that its colour cannot be due to dissociation. It may be remarked, also, that the potash salt in its dry state has remarkable optical properties, which were investigated by Brewster—properties not possessed by the acid.

To the reactions which have been here examined might be added those of methyl-orange, rosolic acid, and other acid indicators. I have found no exception to the rule that the characteristic colours exhibited by these substances, when placed in contact with alkalis, are retained after a thorough desiccation. Also, no acid indicator, when dissociated by a large dilution, shows any tendency to exhibit an anion similar in colour to that of its alkaline compound.

(To be continued).

ON THE EXISTENCE OF CUPRIC SULPHIDE.

By JOHN B. COPPOCK, Harris Institute, Preston.

PROF. MENSCHUTKIN has told us, in his "Analytical Chemistry," that the black precipitate obtained by treating cupric solutions with hydrogen sulphide is Cu_4S_3 , and not CuS , this substance being entirely unknown.

Whether the substance which comes down with hydrogen sulphide is Cu_4S_3 is under investigation, but, as a result of the following investigations, it may be definitely said that cupric sulphide has been prepared, and can always be, by the interaction of a copper salt and hydrogen sulphide, particularly when the copper salt is in excess.

As copper forms such a well-defined cupric oxide, it seemed theoretically certain that such a compound as cupric sulphide should be in existence, knowing the relations of sulphur and oxygen.

Copper sulphate was weighed out in the two following quantities,

0.858 grm. and 0.975 grm.,

and dissolved in water, with the addition of a slight amount of hydrochloric acid, as in qualitative work; hydrogen sulphide was passed to saturate the solution. The precipitate was dried under conditions liable to keep the oxidation of the sulphide to sulphate at a minimum.

Theoretically the two quantities above should give—

0.327 grm. and 0.372 grm.

of CuS ; the precipitates actually weighed—

0.350 grm. and 0.386 grm.

What was the error due to? To the existence in each precipitate of free sulphur, which, when the precipitate was ignited after the final weighing, made itself obvious by burning to sulphur dioxide. This free sulphur was due to the action, as is well known, of the acid solution upon the hydrogen sulphide. In every trial this method gave a precipitate which was polluted with free sulphur, and therefore prevented the preparation of a pure precipitate, whether it was Cu_4S_3 or CuS which came down. The following method was therefore adopted:—Hydrogen sulphide was passed into water; the amount passed in was determined; into this solution a known weight of copper sulphate was put, the weight being more than sufficient to combine with the hydrogen sulphide. There-

fore the solution was saturated with the copper salt. This solution had no added acid, so as to prevent the liberation of free sulphur,—so the only acid present was that due to the liberation of sulphuric by the action going on.

Copper sulphate was thus weighed and added as above.

2.4840 grms.

1.8945 grms.

Each placed in the solutions of hydrogen sulphide containing the following amounts:—

0.1100 grm.

0.1100 grm.

The cupric sulphide thus obtained was certainly a little darker than that obtained by the previous method. The precipitate dried at 100° and with no oxidation weighed—

0.3075 grm. and 0.3076 grm.

These facts were sufficient to show that under these conditions CuS had been prepared.

Turning the CuS into its copper sulphate equivalent, we get—

0.8059 grm.

0.8062 grm.

The copper sulphate, which was left unaltered in the filtrate, was then determined as oxide; the amounts of oxide were found to be—

0.5325 grm.

0.5345 grm.

which are equivalent to—

1.6783 grm. and 1.0886 grm.

of copper sulphate. We therefore get, adding together these separately determined quantities,—

0.8059

0.8062

1.6783

1.0886

2.4842 $\text{CuSO}_4\text{H}_2\text{O}$

1.8948 $\text{CuSO}_4\text{H}_2\text{O}$,

which agree very well with the quantities of copper sulphate which were taken,

2.4840 grms. and 1.8945 grms.,

at the beginning of the investigation.

Here, then, no other formula than CuS will represent the compound formed under these conditions, and so the statement that cupric sulphide is unknown requires modifying.

As regards the alleged Cu_4S_3 , of which more anon, may it not be due to a want of saturating the solution with hydrogen sulphide? Just as in the case of mercury and lead, different compounds of the type MS_2MCl_2 are formed with colour changes, according to the amount of hydrogen sulphide passed in, but which ultimately go to MS completely,

BORON BRONZE.

By H. N. WARREN, Research Analyst.

THIS alloy—or, more correctly speaking, aluminium boron bronze—is brought about by the introduction of aluminium containing boron, not as aluminium boride, but existing as graphite does in cast-iron. Commercially this part of the process is accomplished by heating, in a specially-constructed oxyhydrogen furnace, an admixture of fluor-spar and vitrified boric anhydride, until the dense fumes of boron fluoride commence to appear. At this stage ingots of aluminium are introduced into the liquid mass; reduction at once takes place, with the formation of free boron, which dissolves in the aluminium, rendering it crystalline and somewhat brittle. When this so-prepared aluminium is alloyed with copper to the extent of from 5 to 10 per cent, a bronze is obtained, denser and more durable than ordinary aluminium bronze, and free from brittleness; but the most important property of the alloy is the readiness with which it melts and casts, whereas in the manufacture of aluminium bronze one of the greatest

difficulties is to ensure a uniform mixture. Often a very difficultly fusible alloy of copper and aluminium is formed upon the surface of the already liquid portion, and accompanied by superficial oxidation, thus obstinately refusing to alloy with the remainder. But in the case of the boron compound no such difficulties are met with, the alloy melting perfectly and at lower temperature than when employing pure aluminium. Boron, in fact, seems to have been but little studied, but it is evidently not so serious an enemy to cope with as its halogen silicon, which, when present in minute percentages only, determines the total ruin of the bronze with which it alloys; in other words, it stands almost entirely opposite to other elements, entering into the formation and forming compounds with the most refractory minerals with the greatest ease; for instance, borides of iron, manganese, nickel, cobalt, &c., may be readily formed by the reduction of their accompanying borates in the presence of carbon, whilst those of silver, gold, &c., can only be formed by the introduction of elementary boron into the fused mass; borides of the alkali metals, and even barium and calcium, have been obtained, but boride of mercury still remains unknown,

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CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Concluded from p. 250).

WHEN working in a dark room I obtained the following positions of the line in the flame spectrum; D being 50°00:—

		Difference from the mean.
Metal	65°40	-0°10
	65°25	-0°25
	65°60	+0°10
Chloride	65°60	+0°10
	65°45	-0°05
	65°65	+0°15
Sulphate	65°30	-0°20
	65°45	-0°05
	65°60	+0°10
Nitrate	65°55	+0°05
	65°70	+0°20
	65°40	-0°10
Mean	65°50	

The mean, then, is 65°50, with a mean error of ± 0.125 equal to that found when measuring Fraunhofer's lines. I may say that the measurement of the centre of a brilliant fixed line appears to me to be easier, and susceptible of a greater degree of accuracy, than that of one of Fraunhofer's lines.

To measure the position of the line in the electric spectrum of thallium, I substituted for the fixed blowpipe, successively, a short spark from a coil without a condenser, passing between thick platinum wires terminating in pure iridium balls, well coated either with metallic thallium or its chloride, and a short electric arc, passing between small cones of pure carbon, also well covered with thallium or its chloride. I put the insulated carrier on the right-hand support in front of the collimator, at a suitable height. I arranged the platinum wires, ending in covered balls or carbon cones, horizontally. By working the endless screw of the right-hand support I brought the centre of the interval between the balls or cones into the axis of the collimator, and I marked this support and the table carrying the spectroscope, so that I might always

be able to bring the centre of the interval between the poles to the same position.

Having made the 50th micrometer division coincide with Fraunhofer's D line, the current being previously made by contact of the cones, I brought the cross wires to the centre of the thallium line. Whilst letting the sparks continue, I worked the endless screw of the right-hand support so as to *displace* the balls and cone, in such a manner as to make the thallium line disappear. Then, by means of the endless screw, the centre of the space between the balls and cones was brought to its former position; this was most quickly done by adjusting the support to the marks. I *estimated* the position of the cross wires, which were unmoved, compared with the centre of the re-formed thallium line. Between each displacement and replacement I ascertained, by passing a ray of sunlight, that the 50th scale division coincided properly with Fraunhofer's D line. In a comparatively short time I was able to make the thallium line appear and disappear *five times*, and thus measure the change in the position of the centre of this line.

I have, besides, checked the observations made by this method of ascertaining the displacement undergone by the centre of the line, by repeating the measurement from the moment the line appeared until it disappeared, owing to the gradual movement back and forward of the space between the balls and cones coated with thallium or one of its compounds.

I found thus that, for a distance of 5 or 6 m.m. between the poles, the displacement was insensible for two-thirds of this distance; it was less than the personal error in measuring the position occupied, in comparison with the centre of the line, by the cross-wires which were projected on it in black.

The following are the results of the very fatiguing observations I made in a dark room:—

A. In the centre of the spark, from 3 to 5 m.m. long.

		Difference from the mean.
1st. With metallic thallium	65°60	+0°10
	65°45	-0°05
	65°55	+0°05
	65°40	-0°10
	65°55	+0°05
2nd. With chloride of thallium	65°45	-0°05
	65°60	+0°10
	65°50	+0°00
	65°40	-0°10
	65°65	+0°15

B. In the centre of an electric arc, from 3 to 4 m. m. long.

		Difference from the mean.
1st. With metallic thallium	65°35	-0°15
	65°55	+0°05
	65°60	+0°10
	65°45	-0°05
	65°55	+0°05
2nd. With chloride of thallium	65°70	+0°20
	65°45	-0°05
	65°40	-0°10
	65°55	+0°05
	65°50	+0°00
Mean	65°51	

The mean of the measurements was therefore 65°51, with a mean error of ± 0.085 . The mean of the measurements of the position of the thallium line in the flame spectrum being 65°50, with a mean error of ± 0.125 , I therefore conclude that the position of the thallium lines in the electric and flame spectra are identical.

When using the large Hilger spectroscope with its six Iceland spar prisms, and taking the solar spectrum as a basis of comparison, I found, with absolute certainty, that the positions of the thallium line seen successively in an

oxyhydrogen blowpipe and in an electric arc charged with thallium were identical.

Since these experiments were carried out, and this chapter written, I have had occasion to submit the above observations to a fresh check. Messrs. Liveing and Dewar having kindly put at my disposal the new direct-vision spectroscope designed by them, I was pleased to be able to use this excellent instrument to verify the respective positions of the flame and the electric thallium lines; I found the position of the two lines to be identical.

Thallium thus resembles carbon and potassium, for their flame and electric lines respectively occupy the same position in the spectrum.

In collaboration with M. Depaire I revised the above-described work, and especially the observations on the singleness of the line and the position of the flame and electric thallium spectra, and on the masking of a weak sodium spectrum, in other words, on the non-visibility of the D line under the influence of thallium rays.

We made these observations by using, on the one hand, the metallic thallium and its trioxide, chloride, bromide, nitrate, and sulphate, used during the above-described researches, and, on the other hand, by using some sulphate prepared by M. Depaire.

To carry out this check, we used in succession a single glass prism and a double flint-glass prism spectroscope by M. Duboscq; a double quartz prism instrument by Hilger; an instrument by Hilger fitted with a Chapmann grating; and lastly, the direct-vision spectroscope by Messrs. Liveing and Dewar, the dispersive power of which was equal to the Duboscq spectroscope with its five 60° prisms. Whatever thallium compound we used, whether we examined the flame spectrum in air or the electric spectrum in hydrogen, the results were exactly the same as those described above.

We found that the flame and electric spectra of thallium consisted of a single intense green line, just as described by Bunsen in his "Nouvelles Recherches," and we found the position of this single line in the two spectra to be the same. When using a spectroscope furnished with a grating instead of prisms, we were unable to split up or cause a double reversal of the thallium line.

We checked these results in an electric arc $2\frac{1}{2}$ c.m. long by about 8 m.m. diam., passing between pure carbon electrodes. This check enabled us to make the following observations:—

A. As regards the appearance of the electric arc charged with thallium:—

On dropping into the crater of the arc, by means of a pure carbon needle, some thallium or one of its compounds, such as chloride or sulphate, but preferably a drop of pure metal, it was noticed:—1st, that the deep blue colour of the arc instantly became pale blue; 2nd, that the part of the envelope of the arc which was red, became sparkling white; 3rd, that the pink outer zone of the arc was coloured intense green.

By continuing to introduce metallic thallium into the arc until the air was filled with thallium vapour, which was very dangerous to breathe, we found the preceding observations to be perfectly exact.

At the temperature of the arc, vapour of thallium appears then to be pale or sky blue. The colours of the first and second zone varied with their temperatures, which are below that of the arc.

B. As regards the spectrum of the carbonate charged with thallium:—

At the moment of introducing thallium into the arc, it was noticed that the luminosity of the carbon lines, which varied moreover with the distance between the arc and the collimator, was greatly increased, but that this luminosity was immeasurably inferior to that of the very bright and intense green thallium line interposed between the comparatively pale green carbon lines. The position of the interposed thallium line was exactly the same as that it occupied in the flame and electric thallium spectra. All our efforts to verify the appearance of other lines, on

either side of the green thallium line, properly so called, were in vain. When using the Hilger spectroscope with a Chapmann grating, we could not split up the thallium line or effect the double reversal, a thing which is so easily done with the D line in the electric sodium arc.

Observation of the flame or electric thallium spectrum, by the eye, shows only the single green line. This metal is not susceptible of being dissociated into any other bodies by the forces we have actually at our disposal. It is a true element, as are the other bodies which have been the subject of my investigations.

A REVISION OF THE ATOMIC WEIGHT OF ZINC.*

FIRST PAPER: THE ANALYSIS OF ZINCIC BROMIDE.

By THEODORE WILLIAM RICHARDS
and
ELLIOT FOLGER ROGERS.

(Concluded from p. 251).

Method of Analysis.—Perhaps the best method of explaining the method of analysis is to give a detailed description of a single determination; and for this purpose Analyses 15 and 19, in which both silver and argentic bromide were weighed, will best serve.

The very pure sublimed zincic bromide was pressed into a platinum boat; and the boat was placed in a tube of hard glass, which had been ground into another tube designed to contain a weighing bottle. The apparatus consisted essentially of a combination of the two pieces of apparatus already shown (Figs. 1 and 2); it was devised for a research upon the atomic weight of magnesium now being carried on by Messrs. Richards and Parker, and it will be described in full when that investigation is published. With the help of this apparatus it was possible to heat the zincic bromide to any temperature below its boiling-point in an atmosphere of pure dry air, pure dry carbon dioxide, or pure dry carbon dioxide charged with hydrobromic acid; and these gases could be changed at will merely by the opening and closing of stopcocks. When the heating had been continued for the desired length of time, it was possible to push the boat into the weighing-bottle and to stopper the weighing-bottle very tightly in a perfectly dry atmosphere, without the least chance of the absorption of moisture from the outside air. All the apparatus which could possibly come into contact with bromine or hydrobromic acid was made of glass, with ground-glass joints and glass gridirons for convenient re-filling.

The zincic bromide was heated very gradually at first in an atmosphere of carbon dioxide which had been dried by passing over sulphuric acid, fused zincic bromide, and phosphorus pentoxide. If heated very gradually in this way, zincic bromide may be almost wholly dehydrated without loss of bromine; but a basic bromide is certain to form if the heating is rapid. When all of the apparent water had been expelled from the substance and its containing tube, dry hydric bromide was added to the carbonic dioxide, and the temperature was gradually raised to the fusing-point of zincic bromide. The bromide was kept at a temperature just above its melting point for about an hour; during this time perhaps a tenth of the substance sublimed in the exit end of the "combustion" tube—rendering the drying tube, which had been ground on to protect the exit, unnecessary. It was assumed that at the end of an hour the fused zincic bromide must be as free from water and from basic salt as it was possible to obtain it; accordingly, the temperature was allowed to fall to about 200°, and the current of dry hydrobromic

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*. Presented April 10, 1895.

acid was stopped. Soon air—dried by means of sulphuric acid, fused potash, and phosphorus pentoxide—was substituted for the carbon dioxide, the temperature being allowed to fall to about 150° to avoid any possible decomposition of the zincic bromide; and this current of air was continued for several hours until long after every trace of hydrobromic and carbonic acid had been swept away. In order to "make assurance doubly sure," the whole length of the tube, weighing-bottle and all, was heated to 100° or more several times, in order to prevent any possible occlusion of acid. When all was in readiness, the warm boat was pushed by means of a long glass rod into the weighing-bottle, and the bottle was stoppered with the help of the same rod. The apparatus was then pulled to pieces, the closed bottle was transferred at once to a tight desiccator, and after a suitable rest of several hours, it was weighed with all possible care. The various weighings are tabulated below. (For detailed method see *Proc. Amer. Acad.*, xxviii., 5).

	Common weights, right-hand pan.	Tare : Standard weights, left-hand pan by substitution.	Standard weights corrected.
	Grms.	Grms.	Grms.
Weight of boat beforehand..	7.7693	7.76937	7.76932
" " + bottle ..	19.9757	0.00372	0.00372
The same + ZnBr ₂ after seven hours' cooling ..	25.2389	5.26754	5.26747
After two more hours ..	25.2389	5.26754	5.26747
After two hours' standing in balance ..	—	5.26757	5.26750
Weight of boat after expt. . .	7.7693	7.76938	7.76933
Boat + bottle afterward ..	19.9757	0.00375	0.00375
Gain of boat ..	—	—	0.00001
" " + bottle ..	—	—	0.00003
Average tare of boat + bottle + ZnBr ₂ ..	—	—	5.26748
Average tare of boat + bottle	—	—	0.00373
Weight of ZnBr ₂ in air ..	—	—	5.26375
Correction to vacuum, 20° and 762 m.m. ..	—	—	0.00074
Weight of ZnBr ₂ in vacuum	—	—	5.26449

Before having been treated with water, the bottle and boat were allowed to stand for twenty hours in somewhat moist air. During that time they gained only two-tenths of a m.grm., showing that the diffusion of moisture through the stopper was very slow. In order to prove the efficiency of the drying and fusing apparatus, the bottle with its contents were returned to it, and the stopper was removed by means of a wire, while a current of dry air was allowed to pass through the whole apparatus. This current was continued for half an hour, the boat and bottle being warmed to about 120° . After suitable cooling, the substance was found to have lost one-tenth of a m.grm., being one-tenth heavier than it was in the first place. These weights were not included above, in order to avoid complications; they do not belong necessarily to the analysis, but merely serve to show that the apparatus was wholly sufficient for its purpose.

The boat and its contents were conveyed with great care to a large Bohemian beaker, and the weighing-bottle was rinsed out many times with the purest water. When the zincic bromide had wholly dissolved, the perfectly clear solution was transferred through a large funnel to the glass-stoppered Erlenmeyer flask intended to serve for the precipitation. The boat was easily washed by allowing it to rest in the funnel; and, of course, beaker and all were rinsed with the most scrupulous care. The total

volume of the thus diluted zincic bromide amounted to about 250 c.c.

The silver to be used for the precipitation weighed 5.04328 grms. in the air, or 5.04313 grms. in vacuum. It was dissolved in 10 c.c. of nitric acid, diluted with water, in a large flask provided with a bulb tube, and the absolutely clear solution was freed from lower oxides of nitrogen by standing upon the steam-bath. The contents of the bulbs, usually containing only a few hundredths of a m.grm. of silver, were washed back into the flask, and the whole was diluted to about half a litre.

The addition of the argentic nitrate to the zincic bromide took place in the dark room (see previous papers upon Barium and Strontium), and great pains were taken to prevent exposure of the materials to anything but non-actinic light from this time until the final weighing of the argentic bromide. Of course, every trace of silver was washed into the flask containing the zincic bromide. After the whole had been very thoroughly shaken and allowed to stand for several days, 0.21 c.c. of hydrobromic acid (1 c.c. was equivalent to a m.grm. of silver) failed to produce an evident precipitate, even when the solution was lighted by a brilliant condensed beam of yellow light. On the other hand, 0.60 c.c. of an equivalent solution of silver produced an evident cloudiness; 0.40 c.c. more also produced a cloud. Still, 0.20 c.c. gave a very faint indication of opalescence, after a long time; and, finally, 0.21 gave no trace. On titrating back with hydrobromic acid; it was necessary to add 1.21 c.c. more before the point was reached where an extra 0.20 produced no precipitate. The total amount of silver solution added was then 1.41 c.c., or 0.21 to precipitate the first amount of hydrobromic acid added, 0.21 to show that all the bromine was precipitated, and 0.99 to correspond to the true amount of silver to be added in order to attain the end-point; while the total amount of hydrobromic acid added to reach the end-point in the other direction was 1.42 c.c., an amount which must be subtracted from the amount of silver added. Hence, since the true amount of silver corresponding to the zincic bromide is the mean between the amounts found by titrating in opposite directions (*Proc. Amer. Acad.*, xxviii., 24; xxix., 74; xxx., 384), we obtain it as follows:—

Amount of Silver Required.

	Grms. in vacuum.
Titration with argentic nitrate ..	5.04313 + 0.00099 = 5.04412
Titration with hydrobromic acid ..	5.04313 + 0.00141 - 0.00142 = 5.04312
Average: silver required ..	5.04362

Since it is hardly probable that the end-point may be obtained by this method more nearly than the tenth of a m.grm., the last figure is omitted below.

If, as is probable, the action of silver and hydrobromic acid in preventing the solution of silver bromide resembles the action of silver and hydrochloric in precipitating solutions of silver chloride (Stas), the difference between the end-points 1.00 m.grm. of silver) corresponds to six times the amount of argentic bromide dissolved; that is, this amount must be about $\frac{1}{3}$ or 0.29 m.grm. in 0.85 litre of a solution containing 2 or 3 c.c. of nitric acid and about 5 grms. of zincic nitrate.

In order to precipitate all the bromine, 4 m.grms. more of argentic nitrate were added to the solution, and the whole was very vigorously shaken. After a day or two, the mixture was filtered through a weighed Gooch crucible, and the precipitate was shaken and allowed to stand with many successive portions of water containing 5 m.grms. of argentic nitrate to the litre. It was finally transferred quantitatively to the crucible, washed with pure water to remove the traces of argentic nitrate, and dried at 160° in a porcelain drying oven in a stream of air purified by passing over sulphuric acid and potash. The

2 litres of filtrate were allowed to stand until the shreds of asbestos had settled; and these were collected upon three thicknesses of the best filter paper, ignited, and weighed. The main body of the precipitate was transferred to a porcelain crucible, weighed, fused in a porcelain oven, and weighed again. Below are the data:—

	Standard Common weights by Grms.	Standard weights substitution, corrected Grms.	Standard weights Grms.
Gooch crucible alone	18'4812	0'22840	0'22840
" " + AgBr	27'2633	9'01052	9'01050
Argentio bromide in air	—	—	8'78210
Correction to vacuum	—	—	0'00039
Chief mass of argentio bromide in vacuum	—	—	8'78249
Porcelain crucible + AgBr	25'6757	8'37781	
The same after fusion	25'6755	8'37760	
Loss on fusion	—	0'00021	0'00021
Crucible + ash + asbestos	15'2857	0'05284	
Crucible	15'2853	0'05226	
Ash + asbestos	—	0'00058	
Ash of three filters	—	0'00012	
Asbestos	—	0'00046	0'00046
Total weight of AgBr	—	—	8'78274
Subtract amount corresponding to 1'42 + 0'20 = 1'62 c.c. HBr solution	—	—	0'00282
Argentio bromide corresponding to zinc bromide	—	—	8'77992

Thus, 5'26449 grms. of zinc bromide correspond to 5'0436 grms. of silver and 8'77992 grms. of argentio bromide. If bromine and silver are taken as 79'955 and 107'93 as usual, the atomic weights of zinc computed from these ratios are identical—65'404. Since this is the case, of course the per cent of silver found in argentio bromide $\frac{107.93}{179.885} \times 100$ is identical with that obtained by Stas, or 57'445.

In no one of the other determinations were both silver and argentio bromide determined, hence the others were simpler in execution, although essentially the same in principle. The end-point in Analysis 17 was probably not determined more nearly than two-tenths of a mgrm., while that in Analysis 19 was determined by the nephelometer (*Proc. Amer. Acad.*, xxx., 385) much more accurately even than in the detailed determination. Indeed, this value was so accurate that the hundredths of a mgrm. may have some significance, although the weights taken were so large. The data of all these final determinations are given below:—

FINAL DETERMINATIONS.

The Ratio of Zinc Bromide to Silver.

No. of analysis.	Weight of zinc bromide. Grms.	Weight of silver. Grms.	Ratio. $\frac{\text{ZnBr}_2}{2\text{Ag}}$	Atomic weight of zinc.
14.	6'23833	5'9766	104'379	65'403
15.	5'26449	5'0436	104'380	65'404
16.	9'36283	8'9702	104'377	65'398
Average			104'379	65'402

In this determination the only serious possibility of error is that the zinc bromide may have contained a lingering trace of water in spite of the elaborate precautions adopted to secure its absence. It is hoped that before long a determination of the zinc, as well as of the

The Ratio of Zinc Bromide to Argentio Bromide.

No. of analysis.	Weight of zinc bromide. Grms.	Weight of argentio bromide. Grms.	Ratio. $\frac{\text{ZnBr}_2}{2\text{AgBr}}$	Atomic weight of zinc.
17.	2'65847	4'43358	0'599622	65'410
18.	2'30939	3'85149	0'599606	65'404
19.	5'26449	8'77992	0'599606	65'404
Average			0'599611	65'406
From the first ratio, if O = 16				Zn = 65'402
From the second ratio, if O = 16				Zn = 65'406
Average, if O = 16				Zn = 65'404
If O = 15'96				Zn = 65'240
If O = 15'88				Zn = 64'912

bromine in zinc bromide, may be made in this laboratory, furnishing evidence upon this point. However, since the figure given above agrees closely with the probable corrected result of Morse and Burton's investigation, as well as with the somewhat incomplete determinations of Baubigny, and Gladstone and Hibbert, the value 65'40 may be safely adopted for the present as the most probable value of the atomic weight of zinc.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 21st, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MR. THOMAS B. CASE was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. John Henry Garrett, Cheltenham; Leon Felix Goldstand, 12, Quai Anglais, St. Petersburg; Alfred Griffiths Greenway, Llandrindod Wells, N. Wales; Ernest George Hill, Muir College, Allahabad; Joshua Arthur Hughes, Abercarn, Monmouthshire; Herbert E. Law, 1526, Vallego Street, San Francisco; Asutosh Mitra, Kashmir; Samuel Thomas Skelton, 13, Derby Street, Ramsbottom, near Manchester.

Mr. J. Morrow Campbell is reinstated as a Fellow.

The following papers were read:—

69. "The Diphenylbenzenes. I. Metadiphenylbenzene." By FREDERICK D. CHATAWAY, M.A., and R. C. T. EVANS.

Three isomeric diphenylbenzenes, $\text{C}_6\text{H}_4(\text{C}_6\text{H}_5)_2$ are possible, but up to the present only two compounds having this formula are known,—paradiphenylbenzene, and the so-called isodiphenylbenzene. The constitution of the former is established, as it has been obtained from parabromobenzene, and yields on oxidation paradiphenylcarboxylic acid and terephthalic acid; the constitution of the latter is still doubtful.

The authors have undertaken the synthesis of ortho- and metadiphenylbenzene, and this paper contains an account of the first part of the investigation.

When benzene vapour is led through a red-hot tube, a mixture of hydrocarbons is obtained, and from the portion distilling at temperatures near 400° paradiphenylbenzene and the so-called isodiphenylbenzene have been isolated. This latter, on oxidation, yields chiefly a mixture of benzoic, paradiphenylcarboxylic, and terephthalic acids. No conclusion as to its constitution can be drawn from this, although the fact that its monobromo-derivative yields, on oxidation, an acid which, on reduction, yields diphenyl-

metacarboxylic acid, shows that the phenyl groups probably occupy meta positions.

Having obtained metadichlorobenzene in large amount, the authors have synthesised from this metadiphenylbenzene, which proves to be identical with the isodiphenylbenzene obtained from benzene. The hydrocarbon was obtained by the action of melted sodium on a mixture of metadichlorobenzene and chlorobenzene dissolved in boiling xylene. It is easily separated from the other products of the action by fractional distillation.

Metadichlorobenzene appears to have very slight action on benzene in the presence of anhydrous aluminium chloride, and the hydrocarbon cannot be prepared in this way.

Metadiphenylbenzene is a colourless substance, easily dissolved by ordinary solvents, and crystallising in star-shaped groups of fine needles. It melts at 84° , and boils at about 369° under a pressure of 766 m.m. Its composition and molecular weight, determined by Raoult's method, using benzene as a solvent, agree very closely with those required by the formula $C_{18}H_{14}(C_6H_5)_2$.

70. "Derivatives of Camphoric Acid." By F. STANLEY KIPPING, Ph.D., D.Sc.

The paper contains an account of numerous derivatives of camphoric acid which have been prepared from π -bromocamphoric acid, and some of which have been briefly described in previous notes (*Proc.*, 1895, cxlviii., 33; cli., 88; clvii., 210); the formation, properties, and relation to one another of all these substances are explained on the basis of Bredt's formula for camphoric acid.

The lactonic monocarboxylic acid, $C_{10}H_{14}O_4$ (m.p. 165°), which is produced when an aqueous solution of sodium π -bromocamphorate is boiled, is derived from trans- π -hydroxycamphoric acid, $C_{10}H_{16}O_5$ (m.p. 131°), whereas the more stable isomeride (m.p. 226°) is the lactone of a cis- π -hydroxycamphoric acid, which seems not to exist except in the form of a salt. These lactonic acids are named trans- π -camphanic acid and cis- π -camphanic acid respectively, in order to recall the fact that they are isomeric with, and closely related to the w -camphanic acid, which is derived from w -bromocamphoric acid (*Trans.*, 1896, lxix., 61).

Trans- π -camphanic anhydride, $C_{20}H_{26}O_7$, crystallises in prisms of indefinite melting-point; the isomeric anhydride of the cis-acid crystallises in plates or prisms, melting at 164 – 165° .

Trans- π -camphanamide, $C_9H_{13}O_2 \cdot CO \cdot NH_2$, is obtained when methylic π -bromocamphorate (m.p. 114 – 115°) is treated with aqueous ammonia; it crystallises from aqueous ammonia in transparent octahedra, and melts at 114 – 115° .

Methylic cis- π -camphanate crystallises in prisms melting at 75° . w -Hydroxy-cis- π -camphanic acid, $C_{10}H_{14}O_5$, prepared by oxidising cis- π -camphanic acid with potassium permanganate, separates from water in transparent, hydrated prisms, and melts at 264 – 265° .

w -acetoxy-cis- π -camphanic acid, $C_{10}H_{13}O_5(OAc)$, is formed when the hydroxy-acid is heated with acetyl chloride; it crystallises well, and melts at 123 – 124° .

π -acetoxycamphoric anhydride, $C_{12}H_{16}O_5$, prepared by treating trans- π -hydroxycamphoric acid with acetyl chloride, crystallises in monosymmetric plates, and melts at 86 – 87° (at 89 – 90° on re-heating).

When trans- π -camphanic acid or π -hydroxycamphoric acid is oxidised with nitric acid, it is converted quantitatively into a tricarboxylic acid of the composition $C_{10}H_{14}O_6$ (m.p. 196°), which is named trans-camphotricarboxylic acid; this substance crystallises from water in massive orthorhombic pyramids, and is extremely stable towards ordinary oxidising agents; its formation from π -hydroxycamphoric acid shows that the latter substance contains the group $-CH_2OH$, and consequently the π -substituent in all these π -derivatives has displaced hydrogen from a methyl group.

Trans-camphotricarboxylic anhydride, $C_{10}H_{12}O_5$, forms monosymmetric crystals and melts at 253 – 254° .

Two isomeric lactones are formed when trans-camphotricarboxylic acid is treated with bromine and amorphous phosphorus at 100° and the product then warmed with water; these compounds have the composition $C_{10}H_{12}O_6$, and are both derived from a πw -dihydroxycamphotricarboxylic acid of the composition $C_{10}H_{14}O_7$. The one (β -lactone) crystallises in six-sided plates, and melts at 220° ; the other (γ -lactone) crystallises in flattened needles of indefinite melting-point, and is formed from the isomeride by heating the latter with alkalis and then acidifying.

Cis-camphotricarboxylic acid, $C_{10}H_{14}O_6$, is obtained as a salt when the trans-acid is fused with potash; it crystallises in massive transparent prisms, and has no definite melting-point, owing to the ease with which it is converted into its anhydride.

Cis-camphotricarboxylic anhydride, $C_{10}H_{12}O_5$, is formed when the trans-acid is heated alone or with concentrated sulphuric acid; it crystallises from benzene in prisms which effloresce in the air and melt at 220° .

71. "On some Substances which exhibit Rotatory Power both in the Liquid and Crystalline States." By WILLIAM JACKSON POPE.

Although a very large number of organic substances are known which in the liquid or amorphous condition rotate the plane of polarisation of a polarised ray passing through them, very few crystalline substances are known which exhibit this same property; a still smaller number of substances are known which exhibit circular polarisation both in the amorphous and crystalline condition.

Substances which exhibit circular polarisation when amorphous very frequently crystallise in those crystalline sub-systems in which enantiomorphism is possible, losing during the process of crystallising the power of circularly polarising light; during crystallisation, the latter property is in some way compensated for by the crystalline structure, which has neither planes nor a centre of symmetry. The exact connection between the crystalline form and optical activity of circularly polarising substances is as yet by no means settled, and any remarkable cases of crystallisation of such active substances consequently possess great importance.

Two substances only, viz., matico camphor and rubidium tartrate, are known which possess the power of circularly polarising light in both the amorphous and crystalline states. The author now describes a third case, that of cis- π -camphanic acid, which crystallises in the pyramidal hexagonal system; when viewed between crossed nicols, the hexagonal optic axial picture is seen to be of the peculiar appearance characteristic of circularly polarising hexagonal crystals. The crystals are strongly pyroelectric, and are laevorotatory, the specific rotation being thus of the same sign as that of the amorphous or dissolved substance.

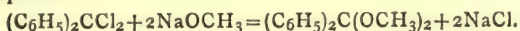
Although so few cases of the occurrence of true circular polarisation in both amorphous and crystalline states are known, a large number of optically active substances are known, the crystals of which do, in parts, exhibit circular polarisation. The latter phenomenon is, however, due to more or less complicated twinning; it is not a result of the actual molecular structure of the crystal, but of the superposition of thin laminae of the crystal. These cases should consequently not be considered as true examples of the occurrence of circular polarisation in the two states. Circular polarisation caused by the piling up of thin plates of biaxial crystals at definite angles to each other has been demonstrated by Reusch, who arranged cleavage flakes of mica one on the other in a definite sense, the optic axial planes of any piece being at 60° to those of the two plates in contact with it; the resulting pile is uniaxial and circularly polarising. A very beautiful example of this kind of circular polarisation is found in the hydrated crystals of the optically active trans-camphotricarboxylic acid (see preceding paper); this substance crystallises in

six-sided plates which simulate hexagonal symmetry, but are really composed of six sectors of an orthorhombic crystal. At the edges of the plates, where no overlapping of the sectors occurs, the biaxial interference figure of the orthorhombic crystal can be seen, whilst in the centre of the plate, where the sectors meet and overlap, the optic axial plane of each sector being at 60° with those of its two neighbours, a uniaxial interference figure is seen and circular polarisation is observed.

The crystals of this substance thus afford a very striking imitation of Reusch's circularly polarising piles of mica plates.

72. "*Dimethoxydiphenylmethane and some of its Homologues.*" By JOHN E. MACKENZIE, Ph.D., B.Sc.

This compound was prepared by the action of sodium methylate on benzophenone chloride, according to the equation—



The chloride was added to the alcoholic solution of the sodium methylate, and after reaction had taken place, the whole was heated in a water-bath for two hours. The substance was obtained pure by re-crystallisation from alcohol, the yield being 81 per cent of the calculated. The crystals are perfectly colourless and odourless, melt at $106.5-107^\circ$, and boil at $288-290^\circ$ without decomposition. They are easily soluble in ether, hot methyl and ethyl alcohols, and benzene, but less so in the cold, insoluble in water. The substance is volatile with steam. It is unaffected by alkalis, but is decomposed by acids, forming benzophenone. In a desiccator over sulphuric acid it loses ether.

Diethoxydiphenylmethane, $(C_6H_5)_2C(OC_2H_5)_2$, is prepared similarly. Yield, 85 per cent of the calculated. The colourless crystals melt at $51.5-52^\circ$. The solubility and general behaviour are similar to the methoxy-compound.

Dibenzoxydiphenylmethane, $(C_6H_5)_2C(OC_7H_7)_2$, is prepared similarly, except that the mixture of chloride and the sodium derivative of the alcohol is heated to $205-210^\circ$. The crystals melt at $104-105^\circ$, and decompose when distilled. They deliquesce on exposure to air. They are easily dissolved by the ordinary solvents when hot, with difficulty when cold.

NOTICES OF BOOKS.

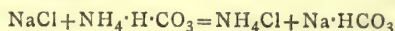
A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali, with the Collateral Branches. By GEORGE LUNGE, Ph.D., Professor of Technical Chemistry at the Federal Polytechnic School, Zurich; (formerly Manager of the Tyne Alkali Works, South Shields). Second Edition, Revised and Enlarged. Vol. III. 8vo., pp. 840. London: Gurney and Jackson (Van Voorst's Successors). 1896.

As the author informs us in his Preface, and as the reader indeed would have no difficulty in discovering for himself, we have here to do not with a new edition in the ordinary sense of the words, but with a new book for which the old edition serves as a basis. The chapters on Ammonia-soda and on the Deacon Process have been entirely re-written, and the section on Electrolysis now appears for the first time.

We read here, what our own experience in several departments of technical chemistry corroborates, that "very few of what practical men take to be important secrets are not accessible in print in one shape or other, or are not known just as well to other practical men." The author has often found that information received as "strictly confidential" was to be obtained in full in the form of patent specifications.

The history here given of the ammonia-soda process is

extremely interesting. The real inventors were undoubtedly H. G. Dyar and J. Hamming, both of London. On June 30th, 1838, they took out an English patent, in which the reaction—



is distinctly set forth. A variety of experiments were made, and one establishment—that of Barker, near Leeds—put alkali on the market for several years. Commercially speaking, the process was a failure, chiefly on account of the loss of ammonia. Solvay's ultimate success depended not on any improvement in principle, but merely on superior mechanical arrangements by which this waste was prevented. Solvay seems to have been under the impression that he had been the first to discover the reaction of the ammonia-soda process. He had, according to Dr. Lunge, "an almost fanatical belief in the enormous value of the process," and was ignorant of the numerous and costly failures already made: had he been aware of the previous career of the invention, he would scarcely have staked his own means and those of his friends on the result. It is here remarked that Solvay's procedures do not present the only solution of the problem. "There exist a number of ammonia-soda works, carried on successfully and profitably, with apparatus differing totally from Solvay's, and preferred by their owners to his, although his patents have now lapsed."

A tabular view here given sums up the respective cost per ton of 58 per cent ammonia-ash and 55 per cent Leblanc ash as £2 18s. 9d. and £3 1s. 1d. This is a very decided advantage for the ammonia process. The repairs in the latter process are very heavy, as ammonia acts upon all iron appliances, upon caoutchouc washers, &c.

In England the consumption of salt for the ammonia process was in 1884 only 80,759 tons, but in 1893 it had risen to 349,609 tons. The great disadvantage of the success of the ammonia process is that it cuts off the supply of cheap hydrochloric acid. Any process which requires such acid is in great peril or has to be abandoned. Instance three procedures for the production of crude aluminium hydrochlorate to be used in the purification of sewage.

Among the almost numberless methods proposed of obtaining alkali, mention is made here (Eng. Pat. 11,008, 1884) of a mixture of nitrate and coal-dust compressed and heated to combustion. The mass is lixiviated, and the solution is brought to crystallisation or converted into bicarbonate by means of the CO_2 obtained by burning the carbon monoxide formed in the first reaction. Our author drily remarks that this invention is probably the outcome of popular evening classes on chemistry, a certain lady having taken out no fewer than three patents in this connection.

The third book treats of the chlorine industry. The great turning-point in the history of the art was Tennant's patent for the absorption of chlorine in dry hydrate of lime. As regards the physiological action of chlorine, we find the statement that persons accustomed to chlorine can tolerate 1 vol. in 10,000 of air. Weigelt finds that 0.005 grm. free chloride per litre kills trout in a few minutes. The use of magnesium chloride as a source of free chlorine has given rise to great hopes and numberless experiments, but hitherto without any marked success. For a long time the exclusive process for obtaining chlorine was the action of hydrochloric acid upon manganese ore or Weldon mud.

All the proposals for recovering the manganese have resulted in failure except those of Dunlop and of Weldon. Of these methods the former has now been practically abandoned.

In the Deacon process for the production of chlorine, manganese is not economised as in the Weldon process, but is entirely superseded.

On page 378 we find a most interesting note, on the uncertainty of all predictions founded on thermo-chemical

data, for which, however, we must refer to the work itself.

In spite of the great advantages of the Deacon process the greatest part of the bleaching-powder made in Britain was in 1895 still produced by the Weldon process.

In Chap. XX., discussing the manufacture of bleaching-powder, the quality of the lime employed is fully insisted on. "Fat lime," such as that of Buxton, is much preferable to poor limes which on slaking yield a gritty powder.

The author protests against the low chambers of 5 feet or lower, as both inhuman to the workman and unfavourable to good uniform working. Cases of the explosive decomposition of bleaching-powder have occurred chiefly when warm bleach has been packed in hot weather.

The fourth book of the work enters very thoroughly into the preparation of alkalis, chlorine, and chlorates by electrolysis.

The author quotes, from the *Chem. Zeitung*, Quincke's discourse on the utilisation of energy when transformed into the electric current. The loss when the steam-engine and the dynamo are used is most serious. Dr. Lunge queries Quincke's assertion that hitherto this is the only source of electricity available in practice. At present he holds that the cheapest source of electricity is water-power, with the dynamo directly coupled on to the turbine. Hence in industry the future belongs to those countries which are rich in water-power. Hurter concludes that "for the production of articles at low price, electrolysis as a manufacturing operation is impracticable." This view was expressed in 1888, but since that time Dr. Hurter has apparently modified his opinions.

In the electrolytic production of soda and chlorine "nearly everything depends upon employing good anodes and diaphragms," and here accordingly is good scope for the inventor.

On the electrolytic methods for the purification of sewage and similar foul waters (Hermite and others), no very decided conclusion has been reached. Two points seem yet open. Is the nitrogenous matter (albumenoid ammonia of Wanklyn or organic nitrogen of Frankland) destroyed or rendered innocuous? Secondly, is magnesia capable of forming a lake with organic matters to the same extent as the oxides of aluminium and iron?

Among the many interesting facts mentioned in the Appendix, we find that at St. Helens each square mile of surface receives the equivalent of 12,036 tons sulphur. The corresponding figures for London being only 11 tons in winter, and 4·4 tons in summer!

A glance at the specifications of the numerous patents quoted or referred to in this volume will be found exceedingly edifying.

That Prof. Lunge has conferred an immense benefit upon chemical manufacturers and analysts, by the production of this his *magnum opus*, will be gladly admitted by every competent reader. We hope that where this has not already been attended to, the three volumes will be forthwith added to the library of every college, technical school, and no less of every chemist (in the continental sense of the term) in all the English speaking countries.

ties of these two constituents expressed in m.grms. per litre. His determinations of nitric acid are made in 4 litres of water evaporated down to a few c.c. When operating upon the water of the Avre he has always been able to complete this concentration in one and the same 2-litre flask. The precipitate is always more or less yellow, like the dry extract containing the nitrates. The water of the Dhuiss is most commonly in the same state as that of the Avre, but the precipitate is of a lighter colour and the dry extract is less yellow. Sometimes it became impossible to evaporate the 4 litres in one flask on account of the violent bumping due to the calcareous deposit, which in such cases was of a pure white, whilst the extract was nearly colourless. In such cases the author divided the water in halves, and boiled them in two flasks until the carbonate was entirely precipitated. He allowed the residues to settle, and evaporated the clear decanted liquids in a third flask.

Condensation of "Black Light."—Gustave Le Bon. —As "black light" possesses several properties which approximate to those of electricity, the author supposed that it might be possible to condense it on the surface of metal plates and then oblige it to traverse the plates so as to act upon photographic plates in darkness, which would place his former experiments in security against all the objections raised against them, especially that of the introduction of light through the chinks of the frames. The author's researches have fully confirmed this hypothesis. He classifies invisible radiations thus:—

X Radiations.—Traverse black paper and organised bodies, but do not traverse most metals; they are neither reflected nor refracted.

Invisible Radiations of Fluorescent Bodies.—Traverse metals as has been shown by D'Arsonval and Becquerel; they are reflected and refracted, and present consequently no property approximating to the X rays.

Radiations arising when Visible Light falls upon Metallic Surfaces.—Our researches show that those radiations traverse neither black paper nor the majority of organised bodies, but traverse a great number of metals. They have also, like electricity, the property of condensing and diffusing themselves on the surface of metals.

Radiations proper to Organised Beings.—Radiations emitted by organisms in darkness, and which enable them to be photographed, as I have shown by operating on ferns, fishes, and various animals. They seem to connect themselves with the radiations of invisible phosphorescence, from which they differ, however, because they do not traverse metallic bodies, those at least upon which I have experimented, especially aluminium.

Action of Hydrobromic Gas upon Thiophosphoryl Chloride.—A. Besson.

Action of Air and of Nitrogen Peroxide upon certain Haloid Compounds of Bismuth.—V. Thomas.—The reactions may be summarised in the following table:—

	Action of Air.	Action of NO ₂ .
BiCl ₃	BiOCl	BiCl ₃ .NO ₂ ; then BiOCl
BiBr ₃	BiOBr	BiOBr
BiI ₃	BiOI; then Bi ₂ O ₃	Bi ₂ O ₃
BiCl ₂	BiOCl	BiOCl

Action of Ethyloxalyl Chloride upon the Aromatic Hydrocarbons in presence of Aluminium Chloride.—L. Bouveault.—The interest of the preparation of the glyoxylic acids of the aromatic series lies in the great ease with which they lend themselves to a crowd of transformations. Claus has shown their easy transformation into substituted phenylglycolic and phenylacetic acids. Gaull has made use of them for the preparation of nitriles by means of hydroxylamin, and the scission observed by Claisen permits us to hope that we may by this means easily prepare the aromatic acids and even the aldehyds.

Novel Method of Separating Naphthylamines.—Marcel Delepine.—Will be inserted in full.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 19, May 11, 1896.

Nitrates in Potable Waters.—Th. Schloesing.—The author thinks that as a first test for distinguishing drainage from springs it is sufficient to determine nitric acid and lime. He gives accordingly a tabular view of the quanti-

Zeitschrift für Analytische Chemie.
Vol. xxiv., Part 6.

Wine Statistics of Germany, VIII.—A view of the production of wine in the different districts of the German empire.

On Sodium Sulpharsenate.—Leroy W. McCoy.—The author concludes from his experiments that there exist no proofs for the existence of free orthosulpharsenic acid.

Determination of Nicotin and of Ammonia in Tobacco.—Dr. Richard Kissling.—A criticism of Vendrödi's paper on the "Determination of Ammonia along with Nicotin" which appeared in the *Zeit. Analyt. Chemie*, xxxiv., p. 413.

Determination of Aniline in presence of small quantities of Toluidine, and of Toluidine in presence of small quantities of Aniline.—F. Dobriner and W. Schranz.—Already inserted.

Determination of Moisture in Aniline, Ortho-, and Paratoluidin.—P. Dobriner and W. Schranz.—The authors have ascertained that the moisture of these bases may be determined in a simple manner. It is merely requisite to determine the consumption of bromonitro-liquid according to Reinhardt (*Zeit. Anal. Chem.*, xxxiii., 89), in equal weights of the undesiccated and the desiccated substances. Let the undried substance consume *a* c.c., the dried *b* c.c.; the moisture *F* may be found by the equation—

$$a : b = (100 - F) : 100,$$

Hence it is indifferent whether the substances in question, independent of the water, are pure, or mixtures of aniline and toluidine, since the proportion of the components is the same in the dried and in the undried substances. Aniline and orthotoluidine can easily be obtained perfectly anhydrous by treatment with ignited potassium carbonate. But if paratoluidin cannot be obtained anhydrous by treatment with fused potassium carbonate at about 50°, and the paratoluidin does not seem to remain quite unaltered after this treatment, at least darker colourations are always obtained. For technical purposes, as commercial paratoluidin contains only minute quantities of aniline, it is sufficient to distil the paratoluidin and to break off the distillation as soon as 10 per cent of distillate have been obtained. The portions remaining in the retort may be regarded as anhydrous.

New Method for Measurements of Temperature.—D. Berthelot.—From the *Comptes Rendus*, cx., p. 831.

Construction and Examination of Normal Mercurial Thermometers.—J. Pernet, W. Jäger, and E. Gumlich (*Zeit. Instrumentenkunde*).—No details are given.

A Mercurial Thermometer which can be Read from a Distance by an Electrical Arrangement.—M. Eschenhagen (*Zeit. Instrumentenkunde*).—The description of the apparatus is too complicated for insertion.

Electrometric Determination of the Final Point in Volumetry.—R. Behrend (*Zeit. Physik. Chemie*).—If we employ a two-cell element with mercurous nitrate and potassium chloride with mercurial electrodes, we observe a strong indication in an electrometer inserted in the circuit. If we add a solution of mercurous nitrate from a burette to the solution of potassium chloride, the electromotive force becomes smaller, and when all the chlorine is precipitated is almost null. Thus, if we use a silver salt and silver electrodes, the percentage of halogens can be ascertained, and in an ammoniacal solution the percentage of iodine along with the other halogens.

A New Colorimeter.—C. Pulfrich.—Hugo Krüss compares this instrument with his own (*Zeit. Anal. Chemie*, xxxiv., 60), and points out both its advantages and defects.

Spectral Apparatus.—C. Pulfrich and F. L. O. Wadsworth.—The former (*Zeit. Instrumentenkunde*) has devised a spectroscope founded on the principle of light returning

upon itself. The latter describes in the same journal a spectroscope slit with a double movement. No details are here given.

Determination of the Melting- and Ignition-point of Explosives.—W. R. Hodgkinson.—(From the *CHEMICAL NEWS*).

MEETINGS FOR THE WEEK.

TUESDAY, 9th.—Medical and Chirurgical, 8.30.

Photographic, 8.

WEDNESDAY, 10th.—Geological, 8.

THURSDAY, 11th.—Royal, 4.30.

Royal Society Club, 6.30.

Mathematical, 8.

FRIDAY, 12th.—Astronomical, 8.

Physical, 5.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1907.

ON THE COLOUR RELATIONS OF ATOMS, IONS, AND MOLECULES.

PART II.

By M. CAREY LEA.
(Concluded from p. 262).

4.—Classification (continued from Part I.).

ANY attempted classification of the elements is necessarily subjected to a severe test through later discoveries. If the classification is in complete accordance with nature, it must offer suitable places for such new elements as may present themselves later. If it does not do this, it must be more or less artificial.

Mendeleeff's remarkable predictions, and the fact that the elements next discovered found places marked out for them in advance, caused his periodic law to be received with enthusiasm. It so happened that these new elements missed the weak portions of the system. This is now much changed. Within the last year or two, several new elements have been discovered for which the periodic law affords absolutely no place.

This appears to be admitted by Mendeleeff. In an article reprinted in the *CHEMICAL NEWS* (vol. lxxii., p. 14), he contends that argon must be polymerised nitrogen, and after examining the possible forms that nitrogen might take, he decides in favour of N_3 .

But Berthelot succeeded in combining argon with carbon disulphide, or with its elements, and from this compound he has been able to regenerate argon with all its characteristic properties. This Berthelot justly calls a capital fact. It is scarcely necessary to say that it is quite fatal to the theory of polymerisation just mentioned.

The impossibility of finding a place for argon in the periodic system will become evident from the following considerations:—If its atomic weight should prove to be 19.9, its place will necessarily be between fluorine and sodium. Introduced into the periodic system, it would take its place at the head of the iron group. It is to be remarked that in the periodic system the iron group is a somewhat singular one. It does not include any of the metals which we commonly associate with iron—cobalt and nickel, chromium and manganese. Instead of these, iron is made to form a group with ruthenium and osmium, so that if argon should enter in the periodic system with the atomic weight of 19.9, it would form the head of a group consisting of argon, iron, ruthenium, and osmium. Or of one consisting of A, Co, Rh, and Ir. Or of another, equally anomalous, A, Ni, Pt, Pd.

But argon may prove to have for its atomic weight the number 39.8. For such an element there is absolutely no place in any periodic system. The position required is already occupied by calcium, and a place cannot be made without dislocating all the following groups—a strong argument in favour of the lower figure.

Helium, with an atomic weight of probably 4, offers equally great difficulties. As the old periodic system excludes hydrogen and commences with lithium, with an atomic weight of 7, any element having an atomic weight less than 7 is, like hydrogen, entirely outside of a system which does not recognise the existence of such elements.

In the system which I have proposed, helium, argon (with the atomic weight of 19.9), and their congeners would constitute a group of their own, taking position between the hydrogen group and the lithium group.

In the first part of this paper, I endeavoured to show that the relations of atoms to the visual rays of the spec-

trum might be made the basis of a classification of the elements composed of these atoms, and that such a classification harmonised extremely well with the known properties of the elements. Not that the particular colour exhibited by an atom has for this purpose any importance; the question is simply whether colour is present or absent—in other words, we have to enquire whether a given atom does or does not exercise selective absorption amongst the visual rays. It was there shown that the atoms of all the elements having atomic weights below 48 did not exhibit selective absorption. After this came two elements which I call transitional, because at some valencies their atoms exhibit selective absorption, and at others do not. Next, elements whose atoms at all valencies exhibit selective absorption. Next came a transitional element and then more elements having colourless atoms, and so on through the entire series of elements arranged in the numerical order of their atomic weights.

It is even probable that the distinction so established between these three classes of elements may eventually prove to have a far-reaching significance, and that those elements whose atoms always exercise selective absorption may prove to be differently constituted in some important way from those whose atoms always allow free passage to all the visual rays.

About the same time that the first part of this paper appeared, Julius Thomsen proposed another and a different system of classification (*Zeit. Anorg. Chem.*, ix., 192), to which later he added a supplement (*Ibid.*, x., 155) in reference to my paper, with the object of showing that the elements which I had indicated as possessing coloured ions were found to come together and to occupy certain distinct positions in his series. This, perhaps, may be taken as additional proof of the conformity of the system which I have proposed to the essential characters of the elements.

A few weeks after the first part of this paper was read before the National Academy (April, 1895), M. Lecoq de Boisbaudran brought before the French Academy a note on the subject of the relations of the elements (*Comptes Rendus*, cxx., 20, May 20, 1895). At page 1100 the elements to which his system of nodes and decrements applies are tabulated. They are thirty-one in number, with three additional elements somewhat widely separated from the rest. I observe that all these thirty-one elements, without an exception, belong to my first division, and have atoms that are colourless at all valencies. The three additional elements belong to the transitional class. The elements of the third division—that is, having atoms coloured at all valencies—find no place in his classification. The chances are enormously against this happening fortuitously. The indications from both this and Thomsen's classification are therefore confirmatory of the principle I have endeavoured to establish: that is, that the presence or absence of specific absorption in a certain range of rays is a function of the atomic weight, and is closely related to the constitution of the elements.

In considering the theory of ionic dissociation it is necessary to bear in mind that no rigorous proof has ever been found for it. It remains, therefore, a theory only; a fascinating theory, because it affords beautiful explanations of phenomena which otherwise have none.

There is, however, an important difficulty connected with this theory. The dissociated ions are often spoken of as "free ions," which, in the absence of exterior electrical agencies, static or dynamic, they do not appear to be. It is certain that, after dissociation, the ions continue in some way to influence and control each other. This fact appears in a great number of reactions, of which the following familiar one may be taken as typical:—

If to a dilute solution of ferrous chloride we add dilute hydrochloric acid in excess, completely excluding the air, there will be a considerable dissociation, and the ferrous ions will be in presence of more than enough chlorine

ions, if these were free, to cause at least some portion of the ferrous ions to acquire additional valency and become ferric ions. No change of the sort can be detected. The chlorine ions which would bring about this change are held in check by the hydrogen ions with which they were previously combined. That this is true is shown by removing the hydrogen ions, which is easily done by the addition of nitric acid. Thereupon those chlorine ions which were previously influenced by, and influenced the hydrogen ions, now influence the ferrous ions, converting them to ferric ions.

The facts of osmosis seem to indicate that dissociated ions are mechanically free, inasmuch as the total number of molecules appears to be increased. But the above reaction, which is one of a great number, shows that in a chemical sense they cannot be considered as free.

Those who, like Ostwald, on the contrary, hold that dissociated ions are perfectly free ("Lehrbuch," 2nd Ger. ed., ii., 783), would perhaps explain the above reaction by the asserted principle that polyvalent ions have a tendency to lose a portion of their valency (*Ibid.*, 796 and 807). One of the examples given (p. 796) is that of the trivalent iron ion which, by reason of its tendency to lose valency, may act as an oxidising agent.

This reasoning does not seem to be sound. Whatever may be the tendency of the ferric ion to lose valency, the tendency of the ferrous ion to gain it is still stronger, so that ferrous chloride acts as a powerful reducing agent by reason of the strong tendency of the ferrous ion to acquire additional valency. This tendency of the ferrous ion shows itself in other ferrous salts, and a similar tendency is exhibited by cuprous and stannous salts. In fact, it may be said that most of our powerful reducing agents owe their activity to the tendency of ions to acquire additional valency; consequently, it cannot be admitted that an opposite tendency prevails. And when, in the above-mentioned reaction, we find that ferrous chloride in dilute solution with hydrochloric acid does not take up additional chlorine ions actually present, in spite of its strong tendency that way, we are compelled to believe that the chlorine ions of the hydrochloric acid, though mechanically dissociated, are still held in check by, and hold in check, the hydrogen ions.

In this connection I may refer to some interesting remarks made by Professor Fitzgerald in his recent Helmholtz Memorial Lecture, reported in *Nature* (January 30, 1896):—"It is almost impossible to explain dynamically the assumption that free electrically charged ions wander about in a liquid in a condition at all rightly described as one of dissociation."

And, again:—"The term dissociation, as applied to electrolytes in which this independence of the ions does not exist, is obviously a misnomer. There is said to be an electrical force acting between the various oppositely charged ions into which a dissolved molecule separates, which in some way binds them. Even in dilute solutions this force is very considerable, and must make the condition of charged ions moving independently in the liquid so unstable as to be dynamically impossible unless other important forces operate at the same time."

From these various considerations, the following conclusions may be drawn:—

1. When highly coloured inorganic substances are composed of colourless ions, then if these substances can be brought into solution, the colour wholly disappears. A number of instances are given above, and no exceptions were met with. Much that is important follows from this. It is proved that the ions have become so far separated that they no longer influence each others' vibration periods. For example, antimony pentasulphide is an intensely coloured substance. It dissolves easily in solution of alkaline sulphides, forming absolutely colourless solutions; because the ions of antimony and of sulphur are colourless, and in the act of solution they separate sufficiently to no longer change each others' vibration periods,

without, however, passing out of each others' spheres of influence. The ion theory is the only one capable of explaining this loss of colour; and, on the other hand, the reactions are so exactly conformable to that theory that they constitute a new proof of its correctness.

2. The union of ions, coloured and colourless, gives rise to the most surprising changes of colour. Two similar coloured ions may unite to form a colourless element. Two similar colourless ions may unite to form a strongly coloured element. No black ion is known. There is absolutely no relation traceable between the colour of an ion and that of the element which it forms.

3. The change of colour of an acid indicator placed in contact with an alkali in no way depends upon dissociation: dissociation may result, but the change of colour is independent of it.

4. Selective absorption of the visual rays by an element can never constitute a basis for classification, but the relation of ions to the visual rays leads to a classification which is in absolute harmony with the chemical characteristics of the elements. It may be mentioned that quite recently two chemists, Thomsen and De Boisbaudran, have proposed new systems of classification, in both of which it appeared subsequently that the elements having colourless ions had come together. And in Thomsen's system the same was also true of the elements having coloured ions.

5. Whilst there is good reason for believing that in solution the ions are separated so as to no longer affect each other's vibrations (see Sec. 1 *supra*), it is also certain that they remain within each other's range of influence, so that they cannot be considered as free. Fitzgerald has shown that this conclusion is in conformity with theory; and experimental evidence has been given above proving that it is also in conformity with fact.

FURTHER NOTES ON THE CHEMISTRY OF THE CYANIDE PROCESS FOR DISSOLVING GOLD.*

By G. A. GOYDER, F.C.S.

Action of Soluble Sulphides in Retarding the Solution of Gold by Potassium Cyanide.

In consequence of a report that the presence of soluble sulphidiss in a cyanide solution greatly retards the rate of solution of gold, the following experiments were made to test this point:—50 c.c. of 0.2 per cent cyanide of potassium was run into a bottle, and 1 c.c. of sulphuretted hydrogen water, and shaken. To this solution a gold leaf was added, and the closed bottle was shaken fifteen minutes continuously, the gold leaf not being perceptibly dissolved.† A little oxide of mercury was then added, and quickly dissolved by gentle shaking. Shook continuously for three minutes, during which all the gold dissolved, and a slight precipitate of sulphide of mercury was formed.

A similar experiment was tried with lead acetate as precipitant of the sulphur instead of mercuric oxide. The action of the lead salt was slower, and a decided excess was required, there being no soluble double cyanide of lead and potassium; consequently the sulphide of lead precipitated was accompanied by much cyanide of lead. By using an excess of the lead acetate, however, the normal action of the cyanide was restored. A solution of mercuric chloride was found as effective as the oxide. A trace of an alkaline sulphide was found to act similarly to sulphuretted hydrogen, and to be removable by the same means.

* From the "Seventh Annual Report of the Council of the South Australian School of Mines and Industries."

† Without the sulphuretted hydrogen water the gold leaf would have all dissolved in about three minutes.

Thiosulphates were found not to interfere with the dissolution of the gold. Agitation with lead carbonate for a moderate time does not remove the sulphur.

The action of the sulphur in the above compounds in retarding the dissolution of the gold is evidently due to the sulphur combining with the oxygen present to form oxygen salts, and to gold not dissolving in aqueous cyanide of potassium containing no free oxygen. As shown above, the sulphur is most quickly and economically removed by the addition of mercuric oxide or chloride. The quantity necessary can be readily determined by a few experiments with gold leaf as above, as the gold is not perceptibly dissolved till all the sulphur is precipitated.

Injurious Effect of Iron in the Zinc Boxes.

In conducting some experiments on the precipitation of gold from cyanide solutions, I noticed that strips of iron and zinc coupled at one end caused a considerable loss of cyanide from the solutions without promoting the precipitation of the gold, but rather retarding it, in consequence of the formation of a precipitate, mostly consisting of cyanide of zinc, on the surface of the zinc. Thus, in one experiment, a solution containing 0.183 per cent of zinc potassium cyanide was divided and put into two flasks, one containing a plate of zinc, the other a similar plate coupled to one of iron. After standing eighteen hours the solutions were analysed. That containing the zinc plate only showed no precipitate, and the quantity of soluble cyanide was 0.183 per cent, no loss having occurred, while the solution in the flask with the zinc and iron plates showed a precipitate, and only contained 0.146 per cent of soluble cyanides, showing a loss of 0.037, or one-fifth of the total amount present at the beginning.

In another experiment with a cyanide solution containing gold, the amount of gold left in solution by the zinc plate alone was 0.0026, while that left with the zinc plate coupled to an iron plate was 0.0042, the amount of gold having been the same in each at the beginning. It is, therefore, evident that iron should be altogether excluded from the construction of the zinc precipitating boxes, and the iron-wire screens frequently used should be replaced by perforated zinc, wood, or other suitable material.

I believe it has already been noted in Africa that the presence of iron screens in the zinc boxes is undesirable.

Selective Action.

A good deal of discussion has taken place on the question of the "selective action" of dilute cyanide solutions for gold. Probably this arises from the indefinite nature of the expression, which appears to have been applied in the first case without an explanation of its precise significance.

It may be defined thus:—The selective action of a dilute cyanide solution in dissolving gold indicates that the ratio of gold to base metal dissolved by a dilute cyanide solution is greater than when a strong solution is used, and consequently less cyanide is wasted by using a weak than a strong solution.

As far as I can understand, "selective action" is only claimed for gold as compared with the minerals and gangue with which it is usually associated, and not for artificial products such as zinc, although to a certain extent it might be applied to that metal. There are at least three ways in which aqueous potassium cyanide acts on metallic minerals:—

1. $4\text{KCy} + \text{Cu}_2 + 2\text{H}_2\text{O} = 2\text{KCuCy}_2 + 2\text{KOH} + \text{H}_2$.
2. $8\text{KCy} + 2\text{Au}_2 + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{KAuCy}_2 + 4\text{KOH}$.
3. $\text{CuCO}_3 \cdot \text{Cu(OH)}_2 + 8\text{KCy} = 2\text{K}_2\text{CuCy}_4 + \text{K}_2\text{CO}_3 + 2\text{KOH}$.

In the first case, that of cyanide of potassium acting on native copper, and in the third, in which cyanide of potassium acts on malachite, the velocity of reaction varies directly as the concentration; but in the second,

in which cyanide of potassium acts on gold, the velocity of reaction is principally governed by the amount of free oxygen present, and, as MacLaren has shown, oxygen is more soluble in rather dilute than in strong solutions of potassium cyanide, and does not appreciably diminish in quantity in very weak solutions; therefore the gold will be dissolved more rapidly in rather weak than in strong solutions, and almost as rapidly in very dilute as in moderately dilute solutions. Therefore it is evident that while a very dilute solution dissolves about as much gold by reaction 2 as a strong solution, it would dissolve much less copper or malachite by reactions 1 or 3 than would be dissolved by strong solutions, and the ratio of gold : copper dissolved by the weak solution would be much greater than that of gold : copper dissolved by the strong solution. The fact that copper is also dissolved according to reaction 2 only modifies the ratio, but does not make the two equal.

As pointed out in a previous report, the gold is also dissolved by some of the double salts formed, such as zinc potassium cyanide, in a somewhat similar manner to that described in reaction 2 above, and, as only metals can react with the double salts in this manner, this would tend to still further increase the quantity of gold dissolved by the very dilute solutions.

If the gold were re-precipitated by any of the minerals present, the "selective action" as above described might be more than counterbalanced; but in the absence of salts which would decompose the cyanides there appears to be no re-precipitation of the gold, provided native metals are not present. A sample of crushed copper ore in large excess was mixed in a bottle with a 2 per cent cyanide solution containing 0.0307 of a grain of gold per 100 c.c., and shaken occasionally during a year, at the end of which time the amount of gold was practically the same as at first, amounting to 0.0306 grain per 100 c.c., an intervening assay giving 0.0307 gold. The above test does not of course prove the statement for all minerals; but taken into consideration with the known characteristics of gold cyanides it appears to me to be almost decisive.

THE REDUCTION OF SELENIC ACID BY HYDROCHLORIC ACID.*

By F. A. GOOCH and P. S. EVANS, Jun.

It has long been known that selenic acid is reducible by hydrochloric acid with evolution of chlorine, but the reaction was regarded as more or less uncertain until Peterson showed (*Zeit. Anal. Chem.*, xii., 287) that conditions of action may be secured under which the reduction proceeds so regularly that the chlorine evolved may be estimated iodometrically and taken as the measure of the selenic acid originally present, or of the selenious acid produced. According to this method of determination, it is only necessary to boil a solution of selenic acid in hydrochloric acid of moderate concentration, and if the solution is not too dilute the reduction is obtained in a few moments. Peterson did not, however, fix with exactness the limits of dilution within which a successful determination of the selenic acid may be expected. The object of this paper is to record the results which we have obtained in studying more closely the conditions necessary to an accurate and rapid reduction. We have used in our experiments solutions of selenic acid prepared by oxidising pure, white, re-sublimed selenium dioxide according to the method laid down in a previous paper from this laboratory (Gooch and Clemons, *American Journal of Science*, vol. I., p. 51) for the quantitative determination of that substance. A portion of the crystalline oxide, approximately 2 grms., was carefully weighed, dissolved in 120 c.m.³ of water

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. I., Nov., 1895.

containing one-twelfth of its volume of sulphuric acid, and treated with a strong solution of potassium permanganate until the colour characteristic of a distinct excess of that reagent prevailed distinctly over that of the brown oxide of manganese thrown down in the oxidation. The liquid was warmed to about 50° C., bleached by oxalic acid, and the excess of this reagent was destroyed by more permanganate. On account of the tendency of manganous salts, when present in considerable amount in warm solutions containing but little free acid, to react upon any considerable excess of permanganate with the deposition of higher oxides of manganese, it is generally necessary to repeat the bleaching and oxidising process two or three times before the final colour of a slight excess of the permanganate remains in clear solution and indicates the completion of the oxidation of the selenium. Finally, the liquid was filtered, diluted carefully to the volume of one litre, and used as a standard solution.

To determine in a general way the point of dilution at which mixtures of selenic and hydrochloric acids yield chlorine, we submitted various mixtures to distillation in a retort arranged with an inverted condenser (so that the aqueous distillate might be constantly returned to the retort) which was joined to an absorption apparatus charged with a solution of potassium iodide. A current of carbon dioxide was passed through the apparatus during the distillation, to carry forward whatever chlorine might be evolved in the process. The iodine liberated in the absorption apparatus was determined by titration with standard sodium thiosulphate. The results of these experiments are given in the accompanying table.

SeO ₃ present. Grm.	Total volume. C.m. ³	Per cent of HCl, sp. gr. 1.20, by volume.	Time in mins.	Chlorine in terms of the theoretical total.
0.1144	100	5	5	None
"	"	10	"	None
"	"	15	"	About 1%
"	"	20	"	" 7%
"	"	25	"	" 30%
"	"	30	"	" 70%

It is plain that so long as the volume of the hydrochloric acid, sp. gr. 1.20, does not amount to more than 10 per cent of the entire liquid no chlorine whatever is evolved, and that only when the percentage of this acid rises as high as 30 does the chlorine evolved during boiling for five minutes approach the theoretical yield. In the ordinary process of distillation, in which the inverted condenser is not used, the liquid must gradually concentrate and the acid become stronger, so that under such conditions the yield of chlorine in a definite period of time must generally be greater than that obtained in the corresponding experiments of the table. Obviously it is advantageous, in attempting the practical reduction of selenic acid, to begin the distillation with acid of strength sufficient to insure the evolution of chlorine in quantity at the outset, and we have found it best to start with a mixture one-third of which is the strongest aqueous hydrochloric acid, sp. gr. 1.20. With solutions so constituted the reduction goes on rapidly. We have found, however, that care must be taken not to prolong the boiling after the solution reaches a concentration corresponding to hydrochloric acid of half strength; for under such conditions—attained in our experiments either by boiling down mixtures of selenious acid and hydrochloric acid, or by making mixtures of selenious acid containing hydrochloric acid of half-strength—we have found that selenium appears visibly in the distillate, while iodine is set free from the iodide in the receiver. Good results may be expected when the mixture, containing one-third of its volume of the strongest aqueous hydrochloric acid at the beginning, is boiled until all chlorine is expelled, care being taken that the volume of the liquid shall not become less than two-thirds of the original volume.

These are conditions which are easily kept; and we have found that from solutions having a total volume of

75 c.m.³ and containing 25 c.m.³ of the strongest aqueous hydrochloric acid (sp. gr. 1.20), the entire amount of chlorine corresponding to the reduction of 0.2 grm. of selenic acid to selenious acid is liberated in ten minutes. The details of these experiments are given in the accompanying table.

Se = 79.1, O = 16.

SeO ₃ taken. Grm.	Total vol. at the outset.	HCl sp. gr. 1.20 present.	Time in mins.	SeO ₃ found. Grm.	Error.
0.0572	75 c.m. ³	25 c.m. ³	10	0.0568	0.0004—
0.0572	"	"	"	0.0569	0.0003—
0.1144	"	"	"	0.1143	0.0001—
0.1144	"	"	"	0.1137	0.0007—
0.1144	"	"	"	0.1147	0.0003+
0.2288	"	"	"	0.2233	0.0005—
0.2288	"	"	"	0.2279	0.0009—

ON THE QUANTITATIVE DETERMINATION OF HYDROGEN BY MEANS OF PALLADOUS CHLORIDE.*

By E. D. CAMPBELL and E. B. HART.

IN the methods heretofore proposed for the quantitative determination of hydrogen in the presence of methane and other paraffins, this element has been estimated from the contraction after complete combustion by explosion with oxygen, or by partial combustion with air and palladium asbestos, or by direct absorption with spongy palladium.

In some cases, where a large amount of gas is available, the mixed hydrogen and paraffins are burned in presence of red-hot copper oxide, the resulting water and carbon dioxide being collected and weighed in the usual manner.

In 1894, F. C. Phillips (*Am. Chem. Journ.*, xvi., 256) proposed the use of palladous chloride, either dry or in solution, as a reagent for the qualitative detection of hydrogen. Phillips has also shown (*Ibid.*, 265—269, and 272) that palladous chloride is reduced by the olefins and by carbon monoxide, which must therefore be removed before testing for hydrogen. The paraffins, he has further shown (*Ibid.*, 262—265), have no action upon palladous chloride, so that hydrogen can be easily detected in their presence. Dr. Phillips proposes the use of dry palladous chloride for the determination of hydrogen, but has not up to the present time overcome the difficulties which he mentions (*Ibid.*, 262).

Thinking it not unlikely that under proper conditions complete absorption of hydrogen might be obtained by means of a suitable solution of palladous chloride, the authors have devised a method based upon this principle, which they have found very satisfactory. This, with Dr. Phillips's permission, they describe below.

A solution of palladous chloride was prepared as follows:—5 grms. of palladium wire were dissolved in 30 c.c. of hydrochloric acid, to which was added 1—2 c.c. of nitric acid. After solution, this was evaporated just to dryness on the water-bath, re-dissolved by adding 5 c.c. of hydrochloric acid (sp. gr. 1.20) and 25—30 c.c. of water, and warming till solution is complete. The solution so obtained was then diluted to 750 c.c., giving a nearly neutral solution, containing about 1 per cent of palladous chloride. This strength of solution was found to be well adapted to the work, and was adopted in our subsequent determinations.

The pipette used in the absorption was the ordinary single Hempel absorption pipette, the only modification being in the clamps which fastened the pipette proper to the stand. In place of the small brass bands generally

* Contributions from the Laboratory of Analytical Chemistry of the University of Michigan. From the *American Chemical Journal*, vol. xviii., No. 4, April, 1896.

used for holding the glass portion in position, three pairs of small screws were substituted, so that the pipette could be easily slipped from between these when desirable, or firmly retained in position by small wires twisted between each pair of screws. In operating, the amount of solution necessary to fill the pipette is first determined and then introduced into the pipette in the usual manner. The gas to be analysed, from which everything but hydrogen, paraffins, and nitrogen had been removed by the usual methods, is then passed into the pipette and followed up by sufficient water to fill the capillary completely. The pipette is then disconnected, after first closing the top with a pinch-cock, removed from the stand, and placed in a water-bath for two hours, at the end of which time absorption will be found complete, unless the amount of hydrogen exceeds 65 c.c., or the pipette has been previously used, in which case a longer time will be required, as will be seen from the experiments cited below.

A pipette should not be used for the absorption of more than about 100 c.c. of hydrogen before re-filling with fresh solution. After absorption is complete, the residual paraffins and nitrogen are passed back, when the residual volume may be measured and paraffins determined by addition of oxygen and explosion in the usual manner. After the pipette has been used for the absorption of about 100 c.c. of hydrogen, the remaining solution of palladous chloride containing precipitated palladium is rinsed into a casserole and then evaporated just to dryness on the water-bath, 5–6 c.c. of hydrochloric acid, and 4–5 drops nitric acid, and a little water are then added and evaporation repeated. The dry palladous chloride so produced is then dissolved by adding 2 c.c. of hydrochloric acid and warming with a small amount of water, and the whole diluted with water to a volume necessary for one pipette full. This solution is then returned to the stock bottle, to be used again when needed.

The accuracy of the above method may be judged from the following experiments. In these experiments all volumes of gases given are those found after reducing to standard conditions, 0° C. and 760 m.m. pressure.

Experiment 1.—

Volume of hydrogen taken = 18.7 c.c.
" nitrogen " = 80.3 "

The mixture was passed over 1 per cent palladous chloride, heated to 50° C. overnight; absorption was complete, residue showing 80.3 c.c.

Experiment 2.—

Volume of hydrogen taken = 53.7 c.c.
" nitrogen " = 23.8 "

1 per cent palladous chloride was used, and heated in water-bath one hour and thirty minutes. Residue = 23.8 c.c. Absorption complete.

Experiment 3.—To the residue of nitrogen from Experiment 2 was added 26.4 c.c. of hydrogen, and the mixed gases returned to the same solution as was used in Experiment 2. Heated in the water-bath one hour and thirty minutes, it still showed 6.2 c.c. of unabsorbed hydrogen. On again returning the gas to the pipette and allowing it to stand over night in the water-bath, absorption was complete, residue again showing 23.8 c.c.

Experiment 4.—

Volume of hydrogen taken = 1.07 c.c.
" nitrogen " = 52.23 "

Heated over 1 per cent palladous chloride in water-bath one hour and thirty minutes, showed absorption of 0.68 c.c. On standing over night in water-bath the absorption was 1.21 c.c.

Experiment 5.—

Volume of hydrogen taken = 1.27 c.c.
" nitrogen " = 70.8 "

This was passed over nearly neutral 2 per cent palladous chloride and heated on water-bath over night, showing an absorption of 1.23 c.c.

Experiment 6.—

Volume of hydrogen taken = 60.2 c.c.
" nitrogen " = 18.2 "

Passed over nearly neutral 2 per cent palladous chloride, and heated in water-bath one hour and thirty minutes. Residue = 18.2 c.c.

Experiment 7.—Residue from Experiment 6 taken, and 64.4 c.c. of hydrogen added. Mixture returned to same solution as that used in Experiment 6, and again heated in water-bath one hour and thirty minutes. 4.4 c.c. of hydrogen still remained unabsorbed, but on returning the gas to the pipette the second time, and allowing it to stand over night, absorption was complete; the residue measuring 18.2 c.c.

From Experiments 5, 6, and 7 it will be seen that a 2 per cent solution of palladous chloride has very little advantage over a 1 per cent solution. Further experiments showed that with strongly acid solutions absorption was retarded.

The most satisfactory results have been obtained by using a fresh 1 per cent nearly neutral solution for each determination; absorption is then complete in two hours. The pipette can be easily re-filled with fresh solution, the one which has been used being evaporated down and re-dissolved and diluted again. 750 c.c. of solution will be found to be plenty to keep two pipettes in use, the amount necessary for filling an ordinary pipette being about 160 c.c.

VALUATION OF BENZIDINE AND TOLIDINE.

By W. VAUBEL.

THE determination of the contents of the benzidine and tolidine bases is best effected, as a matter of course, with nitrite. In addition, the melting-point may be decisive, as for benzidine it will not lie below 125°, and for tolidine not below 120°. But no result useful for the manufacture of the Congo colouring-matters is obtained by the mere determination with nitrite, since the bases still present as an impurity in benzidine and tolidine, which consist of other diphenyl-derivatives, and are important for the purity of the colours in question, are simultaneously titrated. For the determination of these bases, whose diazo- or tetrazo-compounds yield with naphthionic acid no colours which dye cotton directly, the hydrochloric solution of benzidine or tolidine is precipitated with sulphuric acid or a soluble sulphate, and the base remaining in the solution is determined with nitrite. In various commercial products which I examined in exactly the same manner the following quantities of foreign bases were found:—

	Benzidine.	Tolidine.
1.	0.3 per cent	5.0
2.	0.2–0.3	5.0
3.	0.55	2.8

These figures are, of course, applicable only in the same connection as the solubility of benzidine and tolidine sulphate has to be taken into account.

This is for—Benzidine sulphate, 0.0076 gm. benzidine in 1000 water; tolidine sulphate, 0.03 gm. tolidine in 1000 water.

The error thus arising would not be very considerable; so that the precipitation of the sulphuric acid or the sulphate with benzidine might be elaborated as a volumetric method if the solubility of the benzidine and tolidine sulphate were not considerably increased by the addition of hydrochloric acid. Thus there were obtained for benzidine the following values:—

1000 c.c. water—20 c.c. hydrochloric acid (35 p. c.) dissolve 0.02 gm. benzidine.	
" " 50 c.c. dissolve 0.48 gm. benzidine.	
" " 50 c.c. + 100 grms. sodium acetate dissolve 0.45.	

For tolidine sulphate we have the figures:—

1000 c.c. water—20 c.c. hydrochloric acid = 0.513 grm. tolidin.

" " 50 c.c. = 4.42.

Hence a determination of sulphates or of sulphuric acid can yield by this method merely approximate values, and the figures found above for the impurities of benzidine and tolidine are significant in this connection only. In reality, the amount of foreign bases will be much less.—*Zeitschrift für Analyt. Chemie*, vol. xxxv., p. 163.

ON THE

PECULIAR RELATIONS OF SOLUBILITY OF BARIUM SULPHATE.

By R. FRESENIUS and E. HINTZ.

THE authors have made six series of experiments, and summarise the results as follows:—

1. As 4 m.grms. of barium sulphate remain permanently in solution in 400,000 parts of water, whilst 5 m.grms., recently formed, after twenty-four hours occasion a separation, although scarcely perceptible. Hence 1 m.grm. in the nascent state is soluble in about 100,000 parts of pure water.

2. The solubility of barium sulphate in water is most decidedly reduced if the water contains barium chloride or free sulphuric acid, since in their presence 0.5 m.grm. require rather more than 200,000 parts of water for solution, corresponding to the proportion 1 : 400,000 parts; therefore the result to which we are led by the earlier experiments of R. Fresenius.

3. An addition of sulphuric acid decreases the solubility of barium sulphate in water in a rather higher degree than an addition of barium chloride, since the turbidities formed in equal aqueous solutions of barium sulphate formed by sulphuric acid occurred more rapidly and more distinctly than those formed by barium chloride.

4. If barium sulphate separates out of water to which baryta and sulphuric acid have been added in small equivalent quantities, the solution filtered off after twenty-four hours contains in 100,000 parts rather less than 1 m.grm. barium sulphate; for in such filtrates the turbidity occurring on the addition of barium chloride, as of sulphuric acid, rather later than in the solution which had remained clear for twenty-four hours.

(b).—From Series II.

1. As 50 m.grms. barium sulphate remain permanently dissolved in 500 c.c. of an 8 per cent solution of ammonium chloride (at least for seventy-two hours), its solubility in the nascent state in the above-mentioned solution of sal-ammoniac corresponds to the proportion 1 : 10,000 parts.

2. In like manner, its solubility in the solution of ammonium chloride is modified by the addition of barium chloride, and in a far higher degree by an addition of sulphuric acid; for whilst this occasioned a deposition in No. 1 (i.e., in a liquid containing, in 200 c.c., 0.5 m.grm. barium sulphate) there ensued no precipitation, and only a very slight separation in No. 6 (i.e., in a solution containing 5 m.grms. barium sulphate in 200 c.c.). Hence, its solubility in a 10 per cent solution of ammonium chloride in presence of a moderate quantity of sulphuric acid corresponds to the proportion 1 : 400,000; that in presence of a moderate quantity of barium chloride to about 1 : 50,000.

3. Large quantities of ammonium chloride, therefore, do not hinder the precipitation of barium by sulphuric acid, which is always added in excess, whilst they perceptibly interfere with the complete precipitation of sulphuric acid by barium chloride.

From Series III.

1. Whilst 50 m.grms. of barium sulphate remain permanently dissolved in 500 c.c. of an 8 per cent solution of ammonium chloride, this was the case only with 440 c.c. of 2.3 per cent only, for 20 m.grms. corresponding about to the proportion 1 : 22,000. Hence, dilute solution of sal-ammoniac dissolves barium sulphate in a far greater degree than pure water, though not to the same extent as concentrated solutions.

2. In presence of barium chloride, and much more so in that of sulphuric acid, the solubility of barium sulphate decreases considerably in a dilute solution of ammonium chloride, so that the solubility in presence of barium chloride is about 1 : 80,000, and that in presence of sulphuric acid 1 : 400,000.

3. In presence of a moderate quantity of ammonium chloride (2.5 grms. in 100 c.c. of liquid) baryta may be precipitated by sulphuric acid as good as completely; and also sulphuric acid by barium chloride to an extent sufficient for quantitative determinations.

From Series IV.

1. A solution of sodium chloride at 2.3 per cent has a solvent power similar to that of ammonium chloride at 2.3 per cent; therefore, in the former, 440 c.c. remained clear when containing 20 m.grms. barium, corresponding to the proportion 1 : 22,000. On producing 40 m.grms. in the sodium chloride solution there occurred a separation already in ten minutes; whilst in the solution of the ammonium chloride of the same concentration this did not ensue until two hours had elapsed. The solvent power of the latter is, therefore, somewhat greater than that of sodium chloride.

2. On the addition of barium chloride, as well as of sulphuric acid, the same results were obtained as with a solution of ammonium chloride of the same degree of concentration, so that the same conclusions follow in both cases.

Experiments with solutions of sodium chloride at 10 per cent showed that the solvent power of sodium chloride for barium sulphate increases with the concentration as with ammonium chloride. Hence we have a very simple explanation of the fact that muriatic mineral waters not uncommonly contain barium sulphate in solution.

From Series V.

1. As 50 m.grms. of nascent barium sulphate remain permanently in solution in 500 c.c. of nitric acid (at 8 per cent), whilst 100 m.grms. in 600 c.c. of nitric acid at 6.7 per cent give a minimum precipitation only after the lapse of twenty-four hours, the limit of solubility may be assumed at 75 m.grms. in 550 c.c. of nitric acid of 7–8 per cent, corresponding to the proportion 1 : 7300.

2. The solvent power of nitric acid at 10 per cent is considerably reduced by barium chloride, and to a greater degree by sulphuric acid, in an extent increasing with the quantity of the barium chloride or the sulphuric acid, so that from 100 c.c. containing 0.25 m.grm. barium sulphate this body may be eliminated by dilute sulphuric acid, corresponding to the proportion 1 : 400,000; whilst it is separated out by 30 c.c. solution barium chloride only in a solution containing 3 m.grms. in 100 c.c., corresponding about to the proportion 1 : 33,000.

3. Hence, from a 10 per cent solution of nitric acid, baryta can be precipitated as good as completely by a relative excess of sulphuric acid, and sulphuric acid—though less completely—by a relative excess of barium chloride.

From Series VI.

1. The solvent power of hydrochloric acid at 7–8 per cent for barium sulphate is approximately equal to that observed for 7–8 per cent nitric acid, and therefore corresponds approximately to the proportion 1 : 7300.

2. In presence of barium chloride, as well as of sulphuric acid, the solvent action of 10 per cent hydrochloric acid is rather smaller than that of 10 per cent nitric acid, since in 100 c.c. of hydrochloric acid, containing 2 m.grms. barium sulphate, a slight turbidity was occasioned by 30 c.c. solution of barium chloride; whilst in case of nitric acid this does not occur unless 3 m.grms. are present. In 100 c.c. of the hydrochloric acid containing 0.25 of barium sulphate, 4 c.c. of sulphuric acid effected after twelve hours a very slight separation, which did not take place in 10 per cent nitric acid, even if it contained, in 100 c.c., 0.5 m.grm. barium sulphate.

3. It holds good with hydrochloric acid that the solvent power is diminished by barium chloride, as well as by sulphuric acid; the more, the larger is the proportion of the latter.

4. Baryta may be almost absolutely precipitated by an excess of sulphuric acid from 10 per cent hydrochloric, as well as from nitric acid of the same strength. In precipitating sulphuric acid by an excess of barium chloride from such hydrochloric acid, we must remember that in 100 c.c. of filtrate 1 m.grm. barium sulphate remains in solution.—*Zeit. Anal. Chemie*, xxxv., p. 180.

A GENERAL VOLUMETRIC DETERMINATION OF THE METALS PRECIPITABLE BY FIXED CAUSTIC OR CARBONATED ALKALIS.*

By Prof. Dr. RUOSS.

(Concluded from p. 248).

Applications of the Method.

1. *Determination of Alumina in Alums, and of the Free Acid in Aluminic Lyes.*—Mohr, Erlenmeyer, and Löwenstein determine the alumina with litmus as indicator; the two latter authorities employing barium chloride, and, in the case of free acid, with the addition of ammonium-magnesium phosphate—an addition which does not work satisfactorily. Fleischer determines the free acid by adding potassium sulphate, evaporating down, and treating with alcohol. As for the last determination, it may be much more simply effected by methyl-orange. Normal alkali is added until the red changes to orange. For the determination of the former, the solution rendered alkaline is titrated with normal alkali, using phenolphthalein as indicator. If the alum contains salts of ammonium, in presence of which phenolphthalein is not applicable, the ammonia is expelled by boiling with soda, and the liquid is acidified with sulphuric acid, evaporated to dryness, dissolved in water, and titrated.

2. *Determination of Zinc Oxide.*—This determination is effected as follows:—The zinc oxide or zinc carbonate is dissolved in normal hydrochloric acid, and the excess of acid is determined with cupric oxide—ammonia, according to Kieffer's method.

3. *Determination of Hardness of Water.*—This determination with phenolphthalein has the advantage, in comparison of that with oxalic acid, that no filtration and no permanganate solution are necessary, and in comparison with the method of Hefner, that neither filtration nor concentration is required. The procedure is explained by the following examples:—

Measuring Liquids.—Decinormal hydrochloric acid; soda solution, with 4.7364 m.grm. Na_2CO_3 per litre; water, 250 c.c.

Each c.c. of soda solution represents, then, 10 m.grms. per litre; i.e., 1 German degree of hardness and 1 c.c. of hydrochloric acid is equivalent to 1.1174 c.c. of soda solution.

(a) *Permanent Hardness.*—250 c.c. of the water were mixed with 3 drops of phenolphthalein (solution, 1 : 100)

and boiled in a beaker. Soda solution was added by c.c.; at 8 c.c. the liquid was intensely red, even after prolonged ebullition. The liquid was cooled, and hydrochloric acid was added drop by drop, with gentle stirring. The colour was judged by white paper, placed some c.c. beneath the beaker. At 0.6 c.c. hydrochloric acid the liquid was colourless. There were, therefore,—

$$2 \cdot 0.6 \cdot 1.1174 = 1.34 \text{ c.c.}$$

of soda solution to be deducted, and the permanent hardness was therefore 6.7. In the litre there were, therefore, 67 m.grms. lime (calculated as CaO), or 205.8 m.grms. gypsum (calculated as $\text{CaSO}_4 + 2\text{H}_2\text{O}$). If magnesium salts are present, whose carbonate turns the indicator red in the cold, we proceed as for "Precipitation of the Metals as Carbonates."

(b) *Temporary Hardness.*—250 c.c. were mixed in a beaker with five drops of methyl-orange. After adding 7 c.c. hydrochloric acid, the liquid was rose-colour, and after the further addition of 0.4 c.c. soda solution, therefore, there were required, calculated as soda,—

$$7 \cdot 1.174 - 0.4 = 7.42 \text{ c.c.}$$

soda solution. The temporary hardness is, hence, 7.4 per litre; there are, therefore, 74 m.grms. lime (calculated as CaO), or 132.1 m.grms. calcium carbonate (calculated as CaCO_3).

4. *Determination of Sugar by means of Solution of Copper.*—The original volumetric determination of sugar (Fehling's) has now been superseded by the gravimetric method of Allihn. The weighing of the cuprous oxide, reduced in a current of hydrogen, is now almost universal. Instead of this gravimetric method, some other volumetric processes have been proposed, e.g., the permanganate process, which is not quite free from objections; and that of Gentele with potassium-iron cyanide. In the latter it is not easy, in case of coloured liquids, to distinguish the final reaction. Volhard digests the reduced cuprous oxide with nitric acid, adds sulphurous acid and ammonium sulphocyanide, filters, and determines the excess of ammonium sulphocyanate in the filtrate by means of solution of silver. In order to determine the quantity of copper in cuprous oxide we proceed as follows:—The precipitate, together with the glass or asbestos filter, is digested with nitric acid and then evaporated to dryness with sulphuric acid. (If we have a small paper filter the organic substances formed on its evaporation do not prevent the recognition of the end of the process). The residue, which is now neutral, is dissolved in water, and the copper is determined with alkali or baryta-water, using phenolphthalein as indicator. If the alkali is made up so that its standard is 0.31655, and therefore that 1 litre alkali neutralises 19.896 grm. crystalline oxalic acid, each c.c. indicates 10 m.grm. copper. But if the standard of the lye is V, then—

$$1 \text{ c.c. lye} = V \cdot 31.59 \text{ m.grms. copper.}$$

Allihn's tables then show at once the percentage of sugar.

5. *Determination of Sugar by means of Solution of Silver.*—In this process there is the advantage that silver solutions can be titrated with exceptional sharpness by means of solution of sodium chloride.

6. *Determination of Tannic Acid by Precipitation with Copper Acetate.*—The Schroeder-Lowenthal determination of tannin, which was elaborated by a Commission for deciding on a general method for all determinations of tannin, can, like all determinations of tannin, lay no claim to perfection. The fact that in titration it is by no means indifferent whether the permanganate is added rapidly or slowly involves many circumstances which are to compensate the personal factor implicated in working. In particular, the search for the purest possible sort of tannin in commerce, and the determination of its moisture, is a defect which adheres to the method. Even the researches of Katheriner (*Dingler*, ccxxvii., p. 481) on the process of Carpené-Barbieri showed the solution of permanganate as unsuitable. Only the precipitation of

* *Zeitschrift für Analytische Chemie*.

tannic acid by metallic salts seems to me to allow of an exact determination. It is, of course, necessary to remove the objections raised against it. Amongst the many methods I select that of Fleck, who precipitates with cupric acetate, and calculates the tannic acid from the precipitated copper. The first objection which the Commission made to this method is that the reduction factor of tannin for copper has been stated differently by different authorities. But if we reflect that Eder finds the factor 1:3061, and Wolff as 1:304, the error appears quite insignificant, and due to the great diversity of the different kinds of tannin. The further objection relates to the addition of ammonium carbonate, which has a solvent action upon the copper tannate, whilst in its absence the gallic acid is jointly precipitated. This objection can be removed by omitting this addition, and calculating the copper precipitated before and after the precipitation with hide-powder.

Hence the determination of tannic acid is to be conducted as follows:—

1. A portion of the solution of tannic acid is precipitated with copper acetate. The filtrate is evaporated to dryness with nitric acid and sulphuric acid, dissolved in water, and the copper is determined with phenolphthalein and potassa-lye or baryta-water.

(a). Another portion is shaken up with the dry hide-powder, and filtered after eighteen to twenty hours. In one part of the filtrate the copper is determined as directed in No. 1. The difference of the lye consumed multiplied by a factor gives the quantity of the tannin.

The organic substances, tartaric acid, colouring matters, &c., are destroyed by the evaporation with sulphuric acid and nitric acid, yielding, in part, insoluble blackish brown products. The titration in originally strongly coloured substances, such as decoction of oak-bark, is effected with the same sharpness as in pure tannin, as the red colouration of the indicator shows distinctly. The presence of metallic salts in the original solution is of no importance, as we have to do merely with the difference.

The hide-powder of commerce yields to the filtrate only calcium salts, which on evaporation become sulphate, and do not interfere on titration with potassa-lye or baryta-water.

Liquids for Titration.

1. Per litre, 4 grms. pure copper acetate dissolved in the cold, and filtered if necessary.
2. Potassa-lye, decinormal, or baryta-water.

The solution of tannin is to be diluted to 0.2 per cent, or lower. If the filtrate of the first filtration is cupriferous, the dilution is sufficient.

1. 20 c.c. of solution of tannin are mixed with 20 c.c. solution of copper acetate and a little calcium carbonate (approximately to neutrality) in the cold, and filtered. The filtrate is evaporated to dryness with nitric acid and sulphuric acid dissolved in water, and titrated with potassa-lye or baryta-water, using phenolphthalein as indicator.

2. 100 c.c. of the solution of tannin are mixed with 6 grms. of dry hide-powder and filtered after the lapse of eighteen to twenty hours. With 20 c.c. of the filtrate we proceed as in 1.

The difference of the c.c. of lye consumed in 2 and 1 gives if multiplied by 51.682, or 51.682, V the number of m.grms. tannin in 20 c.c. of the dilute solution of tannin. The number 51.682 is obtained from—

$$\frac{79.14}{2} \times 1.3061;$$

1.3061 being the factor taken from the investigations of Eder.

This factor might be established on an investigation of the best qualities of tannin occurring in commerce.

As tannin in alkaline solutions reduces the salts of copper and of silver, we may calculate the quantity of tannin from the quantity of reduced copper or silver before and after the treatment with hide-powder.

NOTICES OF BOOKS.

Argon and Newton: a Realisation. By Lieut.-Colonel W. SEDGWICK (late Royal Engineers), Author of "Force as an Entity," &c. London: W. B. Whittingham and Co. 1896. 8vo., pp. 258.

THE author of the work before us considers that it has distinctly Newton's authority. He informs us, also, that four years before argon was ever heard of he predicted the probable existence of inactive elements, the class to which argon and helium seem to belong. His forecast or prediction is to be found in Chapter III. of his former work, "Force as an Entity," and he was on the eve of pointing it out more formally in an article in the *CHEMICAL NEWS* (vol. lxxi., p. 139).

As a disciple of Newton he recognises the existence of atoms, hard, solid, and unalterable, under any conditions which now obtain. He agrees with Sir John Herschel and Clerk-Maxwell that the atom has "the essential character of a manufactured article," and he further extends this idea by representing argon and helium as "one of the quarries, as it were, from which the materials for our universe were obtained." Though we do not find any formal deliverance on the question, it can scarcely be doubted that Col. Sedgwick does not regard as possible the decomposition of any of our elements or transformation into each other. He regards man as living in a state of open and formal rebellion, as having left his natural abode—the warm, steamy river valleys—and spread into ungenial regions, where he can exist only by the use of artificial heat, of shelter and clothing. He has further changed his diet. Our author seems not to condemn merely the use of animal food, but of grain and of such vegetable matter as requires to be cooked before use. Naturally he should restrict himself, it would seem, to fruits, nuts, and such roots as can be eaten raw, to succulent shoots and buds.

We perfectly admit that untold misery has been occasioned, not to man alone, but to many of his fellow denizens of the globe, by clearing away the forests, and consequently exposing the mountains and uplands to an alternation of flood and drought. But this work has not been due exclusively or mainly to man's greed or folly. The goat, the rabbit, or rather we might say the rodents generally, have taken a prominent part in laying waste some of the most fertile regions of the earth. The war against the vegetable world is waged to a fearful extent by orthopterous insects. If Col. Sedgwick will carefully consider, we think he will find that man's task of "subduing and replenishing the earth" must turn upon extirpating those creatures which seem to devastate and exhaust it. Were we limited to those regions which we can inhabit without artificial heat and without cooked food, our abode would be very circumscribed.

We must admit that Col. Sedgwick's work is replete with matter not merely interesting, but thought-provoking, though we doubt whether many readers will be prepared to accept all his conclusions.

A Dictionary of Chemical Solubilities, Inorganic. By ARTHUR MESSINGER COMEY, Ph.D. (Professor of Chemistry, Tufts College). London and New York: Macmillan and Co. 1896. 8vo., pp. 515.

A DICTIONARY of solubilities is of immense utility at once in the experimental and in the industrial laboratory. The volume before us is the outcome of prolonged and laborious comparison of most of the standard authorities in inorganic chemistry. We say of most, since among the works quoted we find no mention of the works of Watts, of Roscoe and Schorlemmer, and of Würtz. It will further be observed that differences not unfrequently exist among the results given as published by the most

eminent chemists. Thus, barium sulphite is soluble according to Kirwan in 43,010 parts of water, according to Marguerite in 200,000 parts, according to Calvert in 800,000 parts, and according to Fresenius in 400,000 parts. The solubility of lead in distilled water, in water containing carbonic acid, oxygen, presence of gypsum, calcium silicate, magnesium sulphate, old mortar, and sand, lead to great variation in the action of water. For details the readers are referred to the investigations of the Huddersfield Water-Committee of 1886, Messrs. Crookes, Odling, and Tidy, and to the researches of Cornelly (not Cornelly) and Freke published in the *Journ. Soc. Chem. Industry*.

It is very desirable that the solubility of a substance so deleterious as lead, and which has every opportunity of being taken up in public water supplies in consequence of the use of leaden service-pipes, should be placed beyond doubt. Of course a life-time would scarcely suffice for the verification of all the disputed points connected with the solvent action of water upon poisonous matters.

Mr. Comey's work will be recognised as an invaluable laboratory companion; all the more if it were extended so as to include the solubilities of organic bodies.

City and Guilds of London Institute for the Advancement of Technical Education. Report to the Governors, March, 1896. Gresham College, Basinghall Street, London, E.C. 1896.

It has been said that in our modern zeal for education we have begun at the wrong end,—that, instead of furnishing higher instruction to those who needed it and would have turned it to good use, we spent untold millions in forcing elementary education upon those who did not want it, and to whom it has been at best a very doubtful boon. Then, when higher and especially technical training was found to be the real desideratum, we were obliged to appeal to private or casual liberality for the funds required. We are thus competing with ourselves, establishing rival institutions which have substantially the same object. Thus we have the People's Palace, the totality known under the name of South Kensington, the various schools and institutions established by County Councils, &c., as well as the City and Guilds of London Institute, the report of which we are now considering. Now we are not disposed to deny that some of these institutions are doing good work; but are the funds placed at their disposal being laid out to the best advantage? This is a very grave question.

The Council do not omit to put on record the expression of their regret on the death of their late chairman, the Earl of Selborne, to whose energy and devotion much of the growth and prosperity of the Institute is admitted to be owing. The late Professor Huxley is also mentioned as having been an early and valued friend of the Institute.

At the close of last session the diploma of Associate of the City Guilds Institute was granted to forty-seven students, six only of whom had followed the course of chemistry.

A warning is given that, though the electrical industries of the country have opened out a field of employment for well-trained youths, "there have not been wanting signs that the market would soon become over-crowded." It is therefore to be noted with satisfaction that the increase in the day department of the Technical College, Finsbury (210 as against 197 in the previous session), has been more marked in the mechanical and chemical departments than in the electrical department.

Since the close of the first session 431 students have gained certificates, 65 of which are for technical chemistry.

Of the students entered in the evening department, 105 were for chemistry as against 11 in the previous session. Technological examinations were held last year

in 286 towns in the Home Kingdoms, as well as in Sydney, Wellington, Pietermaritzburg, and Bombay.

The total expenditure of the Institute during the past year, in all its branches, has been £30,693 18s. 4d.

This year 46 matriculated third-year students were examined, and 37 were recommended for the diploma of Associate of the Institute; of these six only were for chemistry.

Of the chemical students whose subsequent careers merit notice as real "results," we may mention H. Crompton, Miss A. G. Heath (since dead), R. E. Baker, M. M. Miller, J. Stenhouse, R. W. Sindell, Miss L. E. Walter, E. A. Barnes, W. J. Pope, J. F. Briggs, B. B. Turner, R. L. Jenks, C. Mills, G. C. Jones, O. F. Russell, A. M. Crighton, A. M. Marshall, E. W. S. Schwabe, W. T. Giddon, and E. M. Rich.

The Special Report, by Martin O. Forster, Ph.D., Salters' Company's Research Fellow of the Central Technical College (1895), is well worth a careful study.

We may say, in conclusion, that the City and Guilds of London Institute well deserves the continued and increased support of the public.

Société d'Encouragement pour l'Industrie Nationale, Annuaire pour l'Année 1896. Paris: Chameroy et Renouard.

We have the yearly calendar of the Société d'Encouragement, with a list of the sittings of the Council, of the financial commission, of the committees of the mechanical arts, the chemical arts, the economical arts, the committee of agriculture, that of commerce, of constructions and the fine arts, and of the editorial commission. There are lists of the members of the Society in general, and of each committee.

The latter portion of the book is occupied with the prizes and medals awarded by the Society in 1895, and the prizes for discoveries and inventions to be offered for the years 1897 and 1898.

The Process Year-Book for 1896. An Illustrated Review of all Photo-Mechanical Processes. Conducted by the EDITOR of *Process Work*. London: Penrose and Co., 8A, Upper Baker Street, W.C. Copyright. 8vo., pp. 168.

THE volume before us is at once satisfactory and disappointing, according to the reader's point of view.

To the artist who looks on photography as a method of obtaining representations of persons, of objects, or scenery, accompanied or eked out by mechanical operations, as admitted by the very word "photo-mechanical," it will be satisfactory as an evidence of decided improvement. For the photo-chemist it will be fraught with a reiteration of former failure. For nearly half a century there has been an active search for true method of photography in colours,—some process for obtaining at once, without any "hand-work" etching and the like can produce on the sensitive plate, the reproduction, e.g., of a sunset-sky in its natural colours, and which shall not be liable to fade. The very fact that, after thousands of experiments, we are little, if any, nearer the mark than in the days of Fox Talbot,—the very fact of such prolonged failure is discouraging, and no less so are the attempts at obtaining coloured results in a round-about and partially mechanical manner. Nevertheless, hope and effort should not be abandoned. Some day objects may be reproduced by a pure photo-chemical process, and we may then bow the hand-work out of court.

Many, very many, of the proofs here inserted as illustrations are admirable as far as anything in mono-chrome can so be called. But in most of the illustrations there is an unpleasant omission,—the scenes, events, &c., should have their names added.

Concerning the fidelity of photography something might be said. On pp. 76 and 77 we have a view of Goredale taken from a woodcut, and a view of the same bit of scenery from a photograph. The latter is the more effective as a picture, but the identity of the two is not beyond question. The second view may have been taken when the river was running low, but the very rocks are dissimilar.

It will be perceived that the "Process Year-Book" is something much more than a trade catalogue. It is a rational survey of photographic art, showing at once its achievements, its short-comings, and its desiderata.

Chemical Experiments, General and Analytical. For Use with any Text-book of Chemistry, or without any Text-book. By R. P. WILLIAMS, Instructor in Chemistry, English High School, Boston; and Author of "Introduction to Chemical Science," "Laboratory Manual," &c. Boston, U.S.A., and London: Ginn and Co. 1895. 8vo., pp. 110.

THE peculiarities of this work, as compared with the very numerous class to which it belongs, is the very extensive use made of contractions in the technical terms most commonly occurring—names of appliances and of operations. In this manner a considerable saving of room is of course effected, but the book becomes less easy to read and to understand, and mistakes may more readily be made.

A few uncouth terms are due to the same desire for brevity. Thus a glass measure or graduated glass is here named a "graduate," "Fruit jars" are used for making solutions, and must be distinct from beakers, since both figure in the same list of general apparatus. In a list of chemical elements chromium ranks as a non-metal. The final *e* of such words as oxide, chloride, &c., is amputated, and the pronunciation probably undergoes a corresponding change. But we cannot help asking why an author evidently not afraid of innovation does not go a little further? It would be a distinct gain if, instead of fluorine, chlorine, bromine, we were to write fluor, chlor, brom, amputating at the same time the last syllables of cyanogen and of manganese, which the tyro sometimes confounds with magnesia.

If Mr. Williams, in the probable case of a new edition, would take these hints into consideration, he would confer a real boon on chemists beyond mere economy of space.

E. Merck, Darmstadt. Annual Report on the Year 1895. Published in March, 1896.

THE author or publisher announces that he has added to his factory two new departments—one for the preparation of antitoxin, and the other for the manufacture of remedies from animal organs. With the exception of the so-called anti-vivisectionists and anti-vaccinationists, no one can doubt the potency of certain animal products now being investigated from a therapeutic point of view.

The account here given of the bacteriological department, more especially designed for the preparation of diphtheria antitoxin, is exceedingly interesting and satisfactory. It is less pleasing to find that the wise provision of the German Patent Law, by which its protection was refused to foods and medicines, is, it appears, capable of being evaded.

With rare exceptions Dr. Merck's work is written in idiomatic English, though much of the nomenclature is pharmaceutical rather than chemical.

A compound is here mentioned under the name of *argon*. We need scarcely say that it contains no argon, and should therefore be re-named as early as practicable.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 20, May 18, 1896.

In the nomination of a member for the Section of Rural Economy, *vice* M. Reiset, deceased, M. Muntz received 38 votes out of the total of 53, and was therefore proclaimed elected.

Emission of New Radiations by Metallic Uranium.—Henri Becquerel.—Will be inserted in full.

Preparation and Properties of Uranium.—Henri Moissan.—Will be inserted in full.

Transformation of the Fat into Carbohydrate in the Organism of Animals not supplied with Food.—A. Chaveau.—By animals not supplied with food the author means especially hibernating animals. He holds that the main fact discovered by Regnault and Reiset gives valuable information on the destination of the fats in physiological energetics. It appears that they are chiefly transformed into potential carbohydrates. We cannot otherwise interpret the fixation of oxygen during the winter sleep with the gradual disappearance of fat and the reconstruction of glycogen and of glucose. But nothing warrants us to conclude that this is a process special to hibernating animals.

On certain Properties of the X Rays traversing Ponderable Media.—C. Maltézos.—If we consider the X radiations as hyper-ultra violet radiations, as there is a tendency to admit, I think that we may explain the fact of the absorbent power of bodies as differing with the density on supposing that the index of refraction is not strictly equal to unity, but that, whilst keeping very near to this value, for all bodies it varies from body to body with the density.

Observations on the Reply of MM. Benoist and Hurmuzescu.—Auguste Righi.—In my communication of April 20th I explained the advantages which we realise on enclosing the apparatus producing the X rays in a conductive case not insulated. These advantages are all peculiar to the case where we study the change which these rays produce on a conductor taken in its natural state. As regards the elimination of the electrostatic forces issuing from the tube, it seems to me that any arrangement and that of MM. Benoist and Hurmuzescu are of the same value. But these physicists believe that this elimination is not complete by my method, and believe that they have found in my paper an assertion in favour of their opinion. This assertion does not exist, as will be seen on reading my communication made to the Academy dei Lincei on May 3rd.

Observations on the X Rays.—T. Argynopoulos.—On experimenting with various fluorescent substances on the X rays I have found that potassium and sodium platino-cyanide and also the potassium and lithium platino-cyanide become much more luminous than the corresponding barium salt. The fluorescence of the former was quite visible at the distance of 5 metres, whilst with the same intensity of the X rays the barium platino-cyanide was visible only at a slight distance.

Tubular Generator for Supersaturation with Ozone.—Gaston Seguy.—The author has devised a new ozonising apparatus intended for industrial, sterilising, and therapeutic applications. The construction of the instrument cannot be made intelligible without the large accompanying illustration.

New Electrolyser.—D. Tommasi.—The advantages presented by this instrument may be summarised as fol-

lows:—Polarisation is totally suppressed; the metal which is precipitated on the disk is removed as it is deposited. The density of the different strata of liquid traversed by the current is everywhere the same, thanks to the continuous rotation of the disk.

Researches on Nickel Cyanide.—Raoult Varet.—A thermo-chemical paper not suitable for useful abstraction.

On a Crystalline Barium Tetrachromite.—E. Dufau.—At the high temperature of the arc chromium sesquioxide combines directly with baryta. The compound formed, $4\text{Cu}_2\text{O}_3\text{BaO}$, scratches quartz, is not attacked by acids, and has at 15° the sp. gr. 5.4.

On the Chloraloses.—M. Hanriot.—The compounds obtained are β -galactochloral, $\text{C}_8\text{H}_{11}\text{Cl}_3\text{O}_6$. It forms, on treatment with acetyl chloride in presence of zinc chloride, a tetra-acetylic derivative. With arabinose the author has obtained arabibromal, $\text{C}_7\text{H}_9\text{Br}_3\text{O}_5$.

Certain Symmetric Aromatic Ureas.—P. Cazeneuve and Moreau.—The compounds in question are diparatolylurea and diorthotolylurea.

Relations existing between the Chemical Constitution of Organic Compounds and their Oxidability under the Influence of Laccase.—G. Bertrand.—The oxidability of the different polyphenols under the influence of laccase seems to depend on the ease with which they can be converted into quinones.

Detection and Separation of the Acid Principles contained in Plants.—Will be inserted in full.

Zeitschrift für Analytische Chemie.
Vol. xxxiv., Part 6.

Proving Measuring Flasks, Pipettes, and Burettes.—Morse and Blacklock (*American Chemical Journal*).—This paper, as well as the following one by J. C. Boor, (*Recueil des Travaux Chimiques des Pays-Bas*), on testing measuring vessels, requires the accompanying figures.

A Blast Lamp.—Henry Brearley.—From the *CHEMICAL NEWS*.

New Gas-burner.—F. Allihn (*Chemiker Zeitung*).—This apparatus differs from that of Muencke merely in the flatter form of its cap.

Regulation of Temperature in Desiccation Boxes.—G. Nass (*Zeit. Angewandte Chemie*).—The description of this apparatus is rather obscure.

A Burette with a Specular Back Wall.—Greiner and Friedrich.—This apparatus is said to admit of more accurate readings. In reading, the operator is to look between the graduation and the numbers through towards the back wall, whilst the light is allowed to fall over his right shoulder.

An Absorption Apparatus for Elementary Analysis.—J. Bredt and W. Posth (*Liebigs Annalen*).—The authors recommend a combination of a calcium chloride tube with the soda-lime tubes. The latter are U-shaped, with two small lateral appendages.

A New Reagent for the Detection of Small Quantities of Hydrogen Peroxide.—A. Bach.—From the *Comptes Rendus* (cxix., 1218).

Determination of the Halogens.—P. Jannasch and K. Aschoff propose a direct precipitation of a solution of thallium sulphate (*Zeit. für Anorg. Chemie*). The procedure is founded on the absolute insolubility of thallous iodide in cold alcoholic water, even in the presence of salts of ammonium and other compounds in the solutions of which thallous chloride remains dissolved. The authors proceed as follows:—About 0.5 gm. of a mixture of sodium chloride and potassium iodide are dissolved in 40 to 50 c.c. of water, and mixed with 50 c.c. of a 20 per cent solution of ammonium sulphate and 30 c.c. of alcohol. There was then added a 4 per cent solution of

thallium sulphate until no further precipitation ensues on a further addition. The yellow thallium iodide thus formed quickly settles on the application of a gentle heat. After standing for twelve hours in the cold, the precipitate, with the aid of a suction-pump, is collected on a weighed filter, and is twice washed with a mixture of 5 parts of ammonium sulphate, 70 parts of water, and 30 parts of alcohol, and finally with alcohol 30 to 50 per cent. The filter, with its contents, was dried at 100° and weighed. To determine the chlorine which has remained in solution, the alcohol is first expelled by heating on the water-bath, the residue diluted with water to about 300 c.c., heated to ebullition, and there are added 10 c.c. of concentrated nitric acid and the quantity of solution of silver necessary for precipitation. The liquid must not be allowed to become cold, to avoid a simultaneous precipitation of silver sulphate. The precipitate is therefore allowed to stand for some hours above the flame; the silver chloride is filtered whilst hot, dried, fused, and weighed. This very simple method yields accurate results. Experiments for a separation of bromine and chlorine in a similar manner were unsuccessful, since thallous bromide is in all cases too soluble. Still thallous bromide is so far insoluble in a solution of ammonium sulphate that this behaviour admits of a useful and characteristic detection of a quantity (not too small) of bromine in presence of much chlorine, and of small quantities of iodine in presence of bromine and chlorine.

Artificial Colouration of Sausages.—M. Marpmann (*Zeit. Angewandte Microscopie*).—The author condemns colouration, even with harmless materials, as it conceals the use of decomposing substances. He cuts a disc of the suspected sausage of 1 c.m. in thickness, comminutes it, and covers it with alcohol at 50 per cent. The cellulose and thin parts are then stained by the pigment present, and this colouration can be recognised under the microscope. Any sausage which, after being covered with alcohol at 50 per cent and standing for two hours at the temperature of a room, still appears coloured, must be regarded as suspicious. Those which lose their colour are not artificially coloured.

Determination of Total Residue from the Evaporation of Water.—P. Mason (*Journ. of Anal. Chem.*)—On account of the hygroscopic character of this residue the author effects the evaporation not in a platinum capsule, but in a weighing-glass. For the removal of the stopper, in case it is held down by a vacuum formed on cooling, the stopper is fitted with a small glass cock.

On Cinnamon Bark.—Rudolf Pfister (*Forschungsberichte über Lebensmittel*).—A botanical-anatomical research.

Microscopic Structure of Clothing.—M. Rübner (*Archiv für Hygiene*).—A photographic method of determining the volumes of the pores, and thus showing the absorbent power of the tissues for moisture and the speed of the movements of air within the clothing. Unequal magnitudes of pores distribute the current of air unequally.

Products of Combustion on the Use of the Auer Burner.—M. Gréhaut.—Already noticed under *Comptes Rendus*, clxx., 349.

Examination of "Prepared Tar."—G. Lunge.—"Prepared tar" is a mixture of the pitch of coal-tar with the less valuable portions of the distillation of coal-tar.

On Tritschell's Method for the Determination of Resin in Soaps.—T. Evan and J. E. Beach.—From the *American Chemical Journal* and the *Journal of Analytical and Applied Chemistry*.

Chinese Insect Wax.—Gehe and Co.—This product has a white crystalline texture, resembling spermaceti. It fuses at 82° to 83° . Its sp. gr. at 15° is 0.926, not 0.970 as was formerly stated.

The Examination of Chloroform.—E. R. Squibb (*Pharm. Rundschau*).

The Law of Noble Metals during Cupellation.—R. Oehmichen. — According to the author's experiments these determinations are accurate when the cupellation is conducted within the limits of temperature at which litharge is formed; 620° (the melting-point of aluminium) is a suitable temperature; 900° is too high, and at it the results are too low.

Volumetric Determination of the Phosphoric Acid of Superphosphates, Soluble in Water.—C. Glaser (*Chemiker Zeitung*).

Determination of Nitrogen in Urine.—H. Moreigne (*Bull. Soc. Chim. de Paris*).—If the volumetric determination of nitrogen is to be applied to the decomposition-liquid obtained on Kjeldahl's principle, the addition of mercury must be omitted.

MEETINGS FOR THE WEEK.

TUESDAY, 16th.—Photographic, 8.

WEDNESDAY, 17th.—Meteorological, 7.30.

Microscopical, 8.

THURSDAY, 18th.—Royal, 4.30.

Chemical, 8. "The Action of Bromine on Pinene in reference to the question of its Constitution," by Prof. Tilden, F.R.S. "Note on Santalal and some of its Derivatives," by A. C. Chapman and H. E. Burgess. "The Explanation of some Anomalies in Thermochemistry—Chloral and Bromal Hydrates," by W. J. Pope. "Further Observations on the Production of Chlorine by Heating a Mixture of Manganese Dioxide and Potassium Chlorate," by Prof. McLeod, F.R.S. "The Rotation of Aspartic Acid," by B. M. C. Marshall. "Occurrence of Quercetin in the Outer Skins of the Bulb of the Onion," and "The Colouring Principle contained in the Bark of Myrica nagi (Part I.)," by A. G. Perkin and J. J. Hummel. "Note on some New Derivatives from Camphoroxime," by Dr. M. O. Forster. "Acetylene, its Detection and Ignition in the Air," by Prof. Clowes. Ballot for Election of Fellows.

FRIDAY, 19th.—Royal Institution, 9. "The Utilisation of Niagara," by Thomas C. Martin.

1 Quekett Club, 8.

PHARMACEUTICAL SOCIETY OF GREAT BRITAIN,
17, BLOOMSBURY SQUARE, W.C.

PROFESSOR OF CHEMISTRY.

The Professorship of Chemistry is now vacant, and applications are invited to be sent, together with not more than six testimonials, to the Secretary and Registrar, on or before Tuesday, 23rd inst.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1908.

THE BOYLE LECTURE.

DELIVERED BEFORE THE OXFORD JUNIOR SCIENTIFIC CLUB
ON JUNE 12TH, 1896.

By Professor W. RAMSAY, F.R.S.

(ABSTRACT).

The Position of Argon and Helium among the Elements.

THE discovery of argon and helium, like the discovery of carbon dioxide, of oxygen, and of nitrogen, has brought new problems before the scientific world. To afford an idea of the necessary change of views, the lecturer gave a brief account of the more ancient ideas concerning our atmosphere, and the influence of Boyle, Mahon, Hales, Black, Rutherford, Priestley, Scheele, and Cavendish in modifying and converting these primitive notions of the ancients. Portraits of these investigators were thrown upon the screen. The influence of Lavoisier and of Dalton were touched on, and the overthrow of the phlogistic theory—which predicated that combustible substances, when burned, lost a mysterious principle named phlogiston, instead of gaining oxygen—was alluded to.

Passing on to the more immediate subject of his lecture, Prof. Ramsay shortly described the discovery of argon by Lord Rayleigh and himself, and of helium, accidentally found during a search for a clue to guide him in attempting to form a compound of argon. This element, which up to now had been recognised only by the presence of a yellow line in the spectrum of the solar chromosphere, now appears for the first time as a terrestrial substance. Owing to the non-activity and resistance to combination of these newly-discovered elements, the usual method of determining their atomic weights is not available. Hence purely physical methods had to be resorted to: the density of a gas compared with that of hydrogen, the lightest of all known elements, expresses its molecular weight compared with that of a molecule of hydrogen; and, as a molecule of hydrogen is supposed on substantial grounds to consist of two atoms in chemical union, the density is half the molecular weight, compared, as is usual, with the atomic weight of hydrogen. Not all elements, however, possess molecules consisting of two atoms; among those which possess monatomic molecules is mercury, and this is borne out not merely by considerations connected with the formulæ of its compounds, but also by the ratio between the amount of heat required to raise its temperature when pressure is kept constant on the one hand, or, on the other, when volume is kept constant. Heat, according to the modern conception, may be converted into work, and is therefore termed a form of energy; and the heat communicated to mercury gas, provided it be not allowed to expand, is utilised solely in moving its molecules through space, while with other gases some of the communicated heat is employed in causing the atoms to move in some unknown way, in reference to each other, within each molecule. Both argon and helium display the same peculiarity and behaviour, and it is legitimate to conclude, for the same reason, that in their case, too, molecule and atom are identical. Hence the densities of helium and of argon must be half their atomic weights, inasmuch as atomic and molecular weights are the same. This gives for the atomic weights of these elements the number for helium 4.28, and for argon 39.88. The elements arranged in the order of their atomic weights fall into periods, as shown by Mr. John Newlands some thirty years ago. The

atomic weight of argon, however, is almost precisely that of calcium, and it is unusual to find two elements, and beyond experience to find two such unlike elements, with the same atomic weight. It is therefore necessary to seek for some hypothesis which will remove the difficulty. One is, that argon is not wholly composed of monatomic molecules, but contains, among a great majority of monatomic, a few diatomic molecules. Although this supposition has not yet been absolutely refuted, it appears to be highly improbable. Another supposition is, that argon is a mixture of two or more elements with each other. This idea has lately been put to the proof, and negatived. There is no gas in argon lighter or heavier than 19.94 times the weight of hydrogen.

In conclusion, the lecturer alluded shortly to some of the other remarkable properties of these elements; notably their change of spectrum, with change in electric intensity; the great refractivity of helium, and its extraordinary conductivity for electricity; and lastly, he announced that, contrary to all precedent, it diffuses more rapidly than can be deduced from its density. He predicted that such anomalous behaviour would lead to radical changes in our views concerning the minute structure of gaseous matter.

[Prof. Ramsay announced for the first time, in this lecture, that helium diffuses at a rate considerably faster than would be expected from its density, and thus forms the only known exception to Graham's law of diffusion].

DOES HYDROGEN FIND ITS PROPER PLACE AT THE HEAD OF GROUP I. OR AT THE HEAD OF GROUP VII.?

By Professor ORME MASSON, M.A., D.Sc.

1. THE monad valence of H suits either position equally well. The characteristic valence of the halogens is 1, and the tendency of Cl, Br, and I to exhibit higher valence in oxygen compounds is not exhibited by F.

2. The atomicity of hydrogen (H_2) is the same as that of the halogens. So far as the evidence goes, it seems probable that the alkali-metals are, on the contrary, monatomic in the gaseous and dissolved conditions.

3. The gaseous character of hydrogen and its extremely low boiling-point are just what might be expected from an element heading the group F, Cl, Br, I, but the reverse of what might be expected of an element heading the group Li, Na, K, Rb, Cs. If placed in the former position, hydrogen is in close contiguity to all the other older gaseous elements, viz., N, O, F, Cl. To these may probably be added the new gases He and A, which appear to belong to a new Group, VIII.

4. The atomic weights appear to point to Group VII, rather than to Group I., as the proper place for hydrogen, especially if it be permissible to regard helium as a single element of atomic weight 4. [The spectroscopic evidence to the contrary can hardly be regarded as sufficient till supported by other evidence, and at present this is all in favour of the single element view]. In the first place, the difference between the atomic weight of H (1) and Li (7) is only 6, while that between H (1) and F (19) is 18. The difference found between any other two consecutive elements of the same group ranges from about 15 to 20. A difference of 6 would be quite anomalous, but a difference of 18 well within the rule. In the second place, the difference between the atomic weights of two consecutive elements in the same series varies from rather less than 1 to about $4\frac{1}{2}$; and therefore the order $H=1$, $He=4$, $Li=7$ (showing the first members of Groups VII., VIII., and I. consecutively), is quite in keeping with the rule. If, on the other hand, H be grouped above Li, either six gaps for undiscovered elements must be crowded in between $H=1$ and $He=4$, or He must itself find an intermediate position, say above carbon or nitrogen, with gaps on

either side of it. These alternatives are, to say the least of it, improbable. The following table makes these considerations clear:—

Group..	V.	VI.	VII.	VIII.	I.	II.	III.	IV.
Valence	3	2	1	0	1	2	3	4
			H	He	Li	Be	B	C
			I	4	7	9	11	12
	N	O	F	?	Na	Mg	Al	Si
	14	16	19	? 21	23	24	27	28
	P	S	Cl	A	K	Ca	Sc	Ti
	31	32	35.5	? 37	39	40	44	48

5. If H belonged to Group I, it might fairly be expected to have metallic characters, but not so if it belong to Group VII. From Olszewski's experiments it appears that liquid H is not (as formerly reported) physically a metal. Graham's "hydrogenium" argument, based on the metallic characters of the Pd-H "alloy," might be employed to prove the metallic character of oxygen, which "alloys" with molten silver and with solid platinum (occlusion). Where true combination occurs between hydrogen and a metal, it is doubtful whether the product ever exhibits metallic characters. The combustion of Li in hydrogen to form a white saline-looking powder (LiH), recently discovered by Guntz, is very interesting in this connection; for here H behaves towards Li just as do N, O, and the halogens.

6. The only strong argument for endowing H with metal-like characters is that based upon the study of acids and salts. Here we find hydrogen and metals mutually replacing one another, so that the acids are regarded as hydrogen salts. It may be observed, in passing, that the acids do really form a class apart, for they generally differ in the most pronounced manner from true metallic salts of the same radicle. Nevertheless a clear analogy is here proved between the rôle of hydrogen and that of, say, an alkali-metal in one large and important class of compounds, viz., electrolytes.

7. But the study of a different, though equally large and important, class of compounds brings out an equally striking analogy between the rôle of hydrogen and that of chlorine (or fluorine). I allude, of course, to the organic compounds—hydrocarbons and their alcohols, acids, and other derivatives. Here not only do we find hydrogen and the halogens mutually replacing one another, but we find also that this often takes place with no more effect on the general properties of the compound than is produced by the substitution of one halogen for another.

8. It is quite certain, therefore, that the substitution argument cuts both ways. An inorganic chemist would be most struck with the analogy between hydrogen and the alkali-metals; an organic chemist with the analogy between hydrogen and the members of the chlorine group. In these circumstances it seems fair to allow other arguments to decide the position of hydrogen in the Periodic classification; and these arguments are all in favour of placing it in Group VII., above F, rather than in Group I., above Li.

ON SOME COLLOIDAL COMPOUNDS OF THE RARE METALS.

By M. MARC DELAFONTAINE.

SOME facts have been known for years showing that the rare metals are capable of forming colloidal (or, as some would say, meta-) compounds. For instance, I described in 1863 a very basic ceric nitrate, the aqueous solution of which very much resembles that of dialysed ferric hydroxide and coagulates upon the addition of a small

quantity of nitric acid. Mr. Bahr discovered a similar thorium compound, and I confirmed that fact.

Mr. Damour made known the rare fact that gelatinous basic acetate of lanthanum turns blue when sprinkled with a little powdered iodine,—as starch does. On resuming and extending some old experiments of mine, on this subject, I ascertained that the metals of the yttrium and didymium groups exhibit properties similar to the foregoing. Here is a brief summary of my experiments and their results:—

Owing to the very great difficulty of preparing pure yttrium compounds in large quantity, I first experimented on mixtures of much yttria with little terbia, &c. If, to a moderately strong solution of yttrium acetate, dilute ammonia is added, little by little, there is formed a precipitate which re-dissolves upon stirring. Enough ammonia may be added until the liquid has a faint but decided odour, and turns red litmus blue, and yet no precipitate will be thrown down, even after standing several days. That solution is slightly opalescent; it becomes turbid, and a jelly-like deposit separates when it is boiled; that jelly re-dissolves after cooling, provided the ebullition did not last long.

By dialysis, ammonium acetate was separated. A part of the earthy acetate passed also through the membrane. A clear solution of normal acetate left in contact for many days with yttria, and frequently stirred, gradually dissolves the earth, and makes a colloidal compound identical with that obtained by means of ammonia. After a time, varying from 36 to 72 hours, the remaining fluid exhibited the following characteristics:—

It is transparent, opaline, with a slight fluorescence. It deposits no sediment after standing for a week or more. Its taste is strongly astringent and slightly sweetish. It turns red litmus blue. Its stability is not very great; that is especially the case with long dialysed samples. By boiling, a more or less complete coagulation occurs. The same change will take place at temperatures near 60° C. The solution evaporated at the lowest possible temperature, or in the open air of the laboratory, leaves a transparent gum-arabic-like residue, which does not always re-dissolve integrally in cold water. By calcination the solid chars a little, showing that it retains acetic acid.

In small quantity, dilute oxalic acid coagulates the dialysed solution; in larger quantity, at once, it throws down a bulky pulverulent precipitate of ordinary oxalate.

Didymium, lanthanum, and erbium acetate give products similar to that of yttria; the didymium colloidal solution is less stable than that of yttrium.

Some more facts on these compounds will make the subject of a future note. The foregoing facts show that the rare metals can form soluble colloidal compounds entirely comparable to the so-called soluble alumina and dialysed peroxide of iron, which also retain strongly a small proportion of their original acid.

Linebarger's experiments on colloidal tungstic acid, and supported by other researches, suggest that the above-described substances are highly condensed hydrates. Whether the small proportion of acetic, nitric acid, or chlorine left in the final products, is a mere impurity not separated by dialysis or an inherent component of the molecule—a part of a colloidal- or meta-salt—does not seem to be an answerable question at present.

South Division High School, Chicago, U.S.A.,
June 1, 1896.

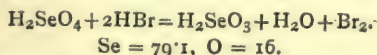
Royal Institution. — A General Monthly Meeting of the Members of the Royal Institution was held on June 1st, Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—William Phipson Beale, Q.C., F.G.S.; Miss Esther Bright; Edward Ball Knobel, Treas. R.A.S.

THE REDUCTION OF SELENIC ACID BY POTASSIUM BROMIDE IN ACID SOLUTION.*

By F. A. GOOCH and W. S. SCOVILLE.

It has been shown in previous papers from this laboratory that potassium bromide may be used with good effect in presence of acid and under well-defined conditions as a reducer of arsenic and telluric acids. This paper gives the results of similar experiments made to test the interaction between the bromide and the selenic acid.

In our experiments we have used selenic acid carefully prepared by oxidising pure, white, re-sublimed selenium dioxide by means of potassium permanganate in the manner described (*Am. Journ. Sci.*, l., 400; *CHEM. NEWS*, lxxiii., 273). When intermixed with sulphuric acid and potassium bromide, selenic acid liberates bromine in proportion to the excess of acid, the bromide, and the elevation of the temperature. When such a solution is boiled the bromine is evolved and may be collected in potassium iodide contained in any appropriate receiver, and the iodine thus set free may be determined by standard sodium thiosulphate and taken as the measure of the bromine distilled. We have found an apparatus previously used in this laboratory in similar work (made by sealing the exit tube of a Voit wash-bottle, used as a retort, to the inlet-tube of a Drexel wash-bottle used as a receiver, with a set of Will and Varrentrapp absorption bulbs sealed to the outlet-tube of the receiver, to serve as a trap) extremely convenient in the distillation process, and a current of carbon dioxide passed slowly through the apparatus aids greatly in carrying the bromine to the receiver and in promoting quiet boiling. We find that the applicability of the reaction to quantitative purposes turns upon the adjustment of the proportions of the reagents used. The following table contains the results obtained by varying the relative amounts of acid and bromide and the time of boiling. The selenium trioxide recorded as found is calculated upon the assumption that selenious acid is the product of the reduction according to the equation—



	SeO ₃ taken as H ₂ SeO ₄ .	H ₂ SO ₄ of half- strength.	KBr taken.	Initial volume.	Final volume.	SeO ₃ found.	Error.
	Grm.	C.m.s.	Grm.	C.m.s.	C.m.s.	Grm.	Grm.
1.	0.1145	5	1	60	25	0.1140	0.0005—
					15	0.1193	0.0048+
2.	0.1145	5	5	60	30	0.1134	0.0011—
					23	0.1184	0.0043+
3.	0.1145	10	1	60	27	0.1134	0.0011—
					23	0.1141	0.0004—
4.	0.1145	20	1	60	35	0.1152	0.0007+
5.	0.1145	20	1	60	35	0.1144	0.0001+
6.	0.1145	20	5	60	45	0.1172	0.0027+

From these results it is apparent that the amount of iodine set free in the receiver is dependent upon the proportion of the bromide, the strength of the acid, and the degree of concentration during the distillation. When the proportions of sulphuric acid, potassium bromide, and selenic acid are favourable, the bromine liberated is removed rapidly to the distillate, leaving the residue perfectly colourless, but as the distillation is continued the liquid residue again takes on colour and more iodine is set free by the action of the distillate upon a clear solution of potassium iodide, while selenium is plainly visible in the receiver. When the amount of potassium bromide is large, its effect is to retain bromine in the liquid so obstinately that no period of colourlessness intervenes before the second stage of colour arrives; when its amount is small while that of the sulphuric acid is also small,

the reduction of the selenic acid and the evolution of the bromine progress slowly; and when the amount of bromide is small, while that of the acid is comparatively large, the interval of colourlessness is prolonged. The proportions which we found best in handling 0.25 gm. of selenic acid, or less, are an initial volume of 60 c.m.³ containing 20 c.m.³ of sulphuric acid of half-strength with 1 gm. of potassium bromide. Under these conditions we find, as in Experiments 4 and 5 of the previous table, that the reduction is almost theoretically exact when the distillation is continued until the re-colouration of the boiling liquid is distinctly recognisable; and this point corresponds in practice very closely to a concentration of volume to 35 c.m.³. In the following table are gathered the results of further experiments in which these conditions of action were preserved:—

SeO ₃ taken as H ₂ SeO ₄ .	H ₂ SO ₄ of half- strength.	KBr	Initial volume.	Final volume.	SeO ₃ calculated.	Error.
Grm.	C.m.s.	Grm.	C.m.s.	C.m.s.	Grm.	Grm.
0.0590	20	1	60	35	0.0588	0.0002—
0.0590	20	1	60	35	0.0591	0.0001+
0.0614	20	1	60	35	0.0616	0.0002+
0.0614	20	1	60	35	0.0607	0.0007—
0.1180	20	1	60	35	0.1177	0.0003—
0.1180	20	1	60	35	0.1180	0.0000
0.1534	20	1	60	55	0.1527	0.0007—
0.2349	20	1	60	35	0.2350	0.0001+

It is plain from these results that, if the conditions of action which we have indicated are observed, the reduction proceeds with regularity sufficient to warrant the use of the reaction as an analytical process.

PHOTOMETRIC METHOD
FOR THE
QUANTITATIVE DETERMINATION OF LIME
AND SULPHURIC ACID.

By J. I. D. HINDS.

THE want of a rapid method of determining with a close approximation the amount of lime and sulphuric acid in drinking water led me to the study of the opacity of fine white precipitates suspended in water. I precipitated in weak solutions lime with ammonium oxalate, and sulphuric acid with barium chloride, then measured the height of a column of the liquid containing the precipitate through which the flame of a common candle was just invisible. I expected only a rude approximation, but to my surprise I found that, between certain limits, an accuracy is attainable equal to that of the ordinary volumetric method.

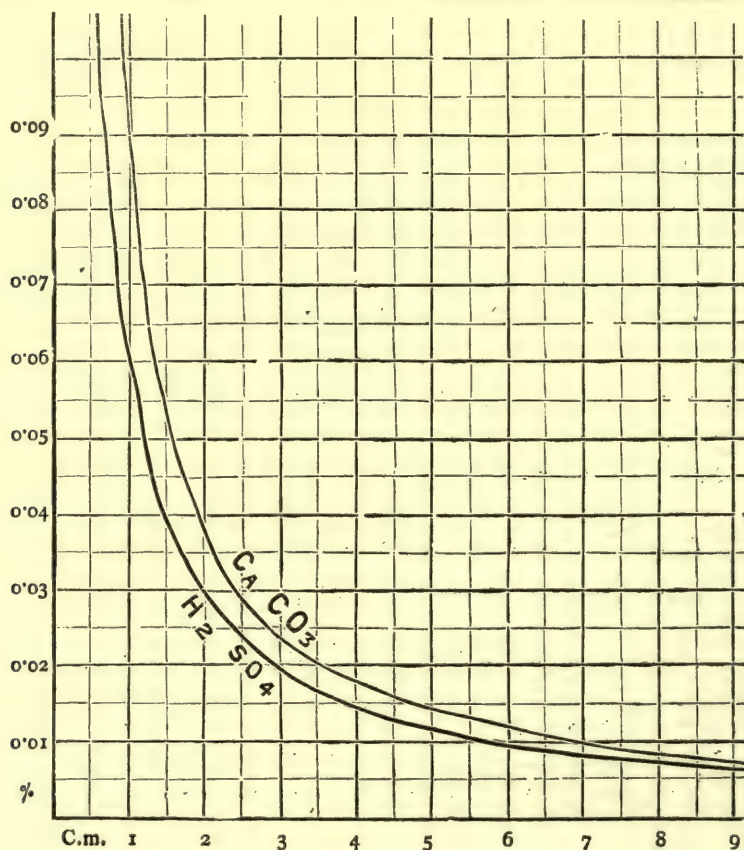
Apparatus.

The only apparatus needed is a cylinder graduated from the bottom in centimetres and tenths. The cylinder should have a plain polished bottom, like Nessler cylinders, and should have a lip at the top. The one I use was made by Eimer and Amend, New York. It is 4 c.m. wide and 20 c.m. high. The graduations run to 18 c.m. This cylinder, however, is not absolutely necessary. A common beaker may be used and the depth of the liquid measured with a small ruler.

The Method.
For Sulphuric Acid.

To determine the values for sulphuric acid I used a decinormal solution whose actual strength was 1 c.c. = 0.00492 gm. H₂SO₄. I took 10 c.c. of this solution, acidulated it slightly with hydrochloric acid, and diluted it to 200 c.c. Of this solution I took 40 c.c., which contained 0.00984 gm. H₂SO₄. To this I added enough solid barium chloride to effect complete precipitation, mixed thoroughly by pouring from beaker to cylinder and

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. l., Nov., 1895.



Equations.

$$\text{H}_2\text{SO}_4 \quad y = \frac{0.0590}{x}$$

$$\text{CaCO}_3 \quad y = \frac{0.0642}{x - 0.3}$$

back, then measured the depth of the column through which the flame was invisible. I then added successive portions of 10 c.c. water, taking the measurement after each addition. The measurement is made as follows:—Hold the cylinder some 12 inches above the burning candle; looking downward through the cylinder, pour in the liquid until the image of the flame just disappears, then read the depth of the liquid. By applying the lip of the beaker to the lip of the cylinder a very gentle stream may be made to flow in. The reading should be made two or three times so as to be sure to read the proper tenth. It is well also to enclose the cylinder in the hand, cutting off the surrounding light, so that the observation may be more accurate.

In this way I obtained the following series of determin-

P.c. H_2SO_4 .	y.	C.m.	C.m.	C.m.	C.m.	x.	x y.
1.	0.0246	2.4	2.4	2.4	2.4	2.4	0.0590
2.	0.0197	3.0	3.0	3.0	3.0	3.0	0.0591
3.	0.0164	3.6	3.6	3.6	3.5	3.575	0.0586
4.	0.0140	4.2	4.2	4.2	4.2	4.2	0.0588
5.	0.0123	4.7	4.8	4.8	4.7	4.75	0.0584
6.	0.0109	5.3	5.4	5.4	5.3	5.35	0.0583
7.	0.0098	5.8	5.9	5.9	5.8	5.85	0.0573
8.	0.0089	6.4	6.4	6.4	6.4	6.4	0.0570
9.	0.0082	6.9	6.9	6.9	6.9	6.9	0.0566
10.	0.0076	7.4	7.5	7.5	7.5	7.475	0.0568
11.	0.0070	8.0	8.0	8.1	8.1	8.05	0.0564
12.	0.0066	8.6	8.6	8.7	8.7	8.65	0.0570

ations. The strength of the solutions is expressed in per cent of H_2SO_4 , and is represented by y. Column 1 gives the number of the solution; col. 2 the per cent of H_2SO_4 ; cols. 3, 4, 5, and 6 give the depths of the liquid in c.m. and tenths for four series of observations; col. 7 contains the means of these depths, expressed also by x; col. 8 contains the products of these means by the percentage, represented also by xy.

I found that the continued agitation and dilution of the solutions seemed to increase the opacity, though very slightly. So I made another series with solutions more dilute, with the following result.

Second Series.

P.c. H_2SO_4 .	y.	C.m.	C.m.	C.m.	C.m.	x.	xy.
1.	0.0098	6.1	6.1	6.0	6.1	6.075	0.0595
2.	0.0089	6.6	6.7	6.6	6.6	6.625	0.0589
3.	0.0083	7.2	7.3	7.3	7.3	7.275	0.0597
4.	0.0075	7.9	7.9	7.9	7.9	7.9	0.0592
5.	0.0070	8.5	8.5	8.4	8.4	8.45	0.0591
6.	0.0066	9.0	9.1	9.1	9.1	9.075	0.0598
7.	0.0061	9.6	9.7	9.7	9.7	9.675	0.0590
8.	0.0058	10.2	10.2	10.2	10.2	10.2	0.0591
9.	0.0055	10.8	—	—	10.8	10.8	0.0594

Mean value of xy 0.0593

Mean value of xy for the first six of

First series 0.0587

Mean of the two 0.0590

We observe that the product xy , that is the number obtained by multiplying the per cent of sulphuric acid in the solution by the depth of the column through which the flame is just invisible, is a constant, and that the curve made by taking the one as the ordinate and the other as the abscissa is an hyperbola referred to its asymptotes, of which the equation is—

$$xy = 0.0590;$$

This is represented by the lower curve in the accompanying diagram. Solving the equation for y , we have—

$$y = \frac{0.0590}{x}$$

To find the amount of sulphuric acid in any solution, observe the value of x , divide it into 0.0590; the quotient will be per cent. Or remove the decimal point three places to the right and we have parts in 100,000. For example, suppose the depth observed is 5.0 c.m.; the quotient is 0.0118. The solution therefore contains 0.0118 per cent of sulphuric acid, or 11.8 parts in 100,000.

For SO_3 the equation is—

$$y = \frac{0.0482}{x}$$

In the above example the amount of SO_3 is 0.00965 per cent, or 9.65 parts in 100,000.

Probable Error.

To determine the probable difference between the observed and computed values, we may compare the second set of observations above with the percentages calculated from the equation. In the following table the first column contains the observed depths of the liquid; the second gives the actual strength of the solution used; the third gives the numbers calculated by the equation; the fourth contains the difference; and the fifth the square of the difference between the numbers of the two preceding columns. This difference is represented by v .

C.m.	Per cent used.	Per cent calculated.	v .	v^2 .
6.0	0.0098	0.0098	0.0000	0.00000000
6.6	0.0089	0.0089	0.0000	0.00000000
7.3	0.0082	0.0081	0.0001	0.00000001
7.9	0.0075	0.0075	0.0000	0.00000000
8.5	0.0070	0.0069	0.0001	0.00000001
9.0	0.0066	0.0065	0.0001	0.00000001
9.7	0.0061	0.0061	0.0000	0.00000000
10.2	0.0058	0.0057	0.0001	0.00000001
10.8	0.0055	0.0055	0.0000	0.00000000

Sum Σv^2 0.00000004

By the method of least squares, the probable error, r , is obtained by the equation—

$$r = 0.6745 \sqrt{\frac{\Sigma v^2}{n-q}}$$

in which n = the number of observations, in this case nine, and q the number of constants in the equation, in this case one. The equation becomes—

$$r = 0.6745 \sqrt{\frac{0.00000004}{8}} = 0.00005$$

The probable difference, then, is 0.00005 per cent, or one part in 2,000,000.

(To be continued).

ACIDIMETRIC ESTIMATION OF VEGETABLE ALKALOIDS. A STUDY OF INDICATORS.*

By LYMAN F. KEBLER.

THE titration of alkaloids with volumetric acid solutions has been evolved from the study of the basicity of the alkaloids on the one hand, and from their behaviour with indicators on the other. The method appears to have been developed somewhat spasmodically from quite an early period. As early as 1846 M. Schloëssing (1846, *Comptes Rend.*, xliii., 1142; 1847, *Ann. Chim. Phys.* [3], xix., 230; *Chem. Gaz.*, v., 41; *Am. J. Pharm.*, xix., 68) proposed the method, and applied it to the titration of nicotine with a view of establishing its equivalent, using sulphuric acid and litmus in his work. Sixteen years later the work was taken up by Wittstein (1862, *Vierjahrsschr. Prakt. Pharm.*, xi., 3 51), who was followed by F. M. Brandl (1864, *Vierjahrsschr. Prakt. Pharm.*, xlii., 322), Liecke (1865, *Mittheilungen des Hannov. Gew.-Ver.*, p. 160; *Ding. Poly. J.*, clxxviii., 235; *Polyt. Notizbl.*, No. 20; *Zeits. Anal. Chem.*, iv., 492), Kosutany (Kosutany, "Anal. Bestim. einiger Bestandth. d. Tabakspflanze. Diss. Altenburg, Hungary"), and G. Dragendorff (1874, "Chem. Werthbestim.", pp. 42 and 55; see also "Plant Analyses," 1884, Eng. ed., pp. 63 and 188). Up to this time nicotine and conine were the only alkaloids operated on, and litmus the only indicator employed. In 1879 L. van Itallie (1879, *Nederland. Tydschr. v. Pharm.*, Jan.; *Analyst*, xiv., 118) extended the work to several other alkaloids, using iacmôid as indicator. A. W. Gerrard (1882 and 1884, *Year-book of Pharm.* pp. 401, 447), a few years later, employed litmus and phenolphthalein in titrating the alkaloids of belladonna. From the contributions of O. Schweissinger (1886, *Pharm. Centralhalle*, xxvii., 492), who used cochineal as indicator, and those of E. Dieterich (1887, *Pharm. Centralhalle*, xxviii., 21; *Pharm. J. Trans.* [3], xvii., 888; *Am. J. Pharm.*, lix., 179) and P. C. Plugge (1887, *Arch. d. Pharm.* [3], xxv., 45, 49; *J. de Pharm. et de Chim.* [5], xv., 571; *Ber. d. Chem. Ges.*, xx., 148; *J. Chem. Soc.*, lii., 621) we may ascribe the impetus which the titration of alkaloids with volumetric acid solutions received at the beginning of the present decade.

The method had been gaining ground rapidly when several most valuable communications appeared by C. C. Keller (1892, *Schweiz. Wochenschr. f. Chem. u. Pharm.*, xxx., 501, 509; *Am. J. Pharm.*, lxxv., 78; 1893, *Schweiz. Wochenschr. f. Chem. u. Pharm.*, xxxi., 473; *Ztschr. Oesterreich-Apotheker*, xlvii., 563, 586; *Am. J. Pharm.*, lxxvi., 42), of Zurich, since which great improvement has been made.

In volumetric analysis, the first question demanding attention is a suitable indicator or delicate end reaction.† The object of this communication is to present the results of a study of five indicators in titrating alkaloids, thinking perhaps it may be of some service in formulating systematised methods of analysis in alkaloidal chemistry. The discordant results of analysis often obtained by different chemists operating on the same sample are greatly to be regretted. It is the writer's opinion that the discrepancies are chiefly due to differences in *modus operandi*, to defective apparatus, and, in volumetric analysis, to different end reaction tints arbitrarily assumed by each worker.

In order to eliminate the factors of uncertainty as completely as possible, the methods of operation were carefully written out and closely adhered to in all the work. The burettes and a pipette were carefully calibrated in order to ascertain the necessary factor for correction.

* Read at the Springfield Meeting. From the *Journal of the American Chemical Society*, vol. xvii., No. 10, October, 1895.

† Alkaloids, generally, are neutral to phenolphthalein; consequently it cannot be employed in titrating alkaloids directly. It is available for indirect titrations, i.e., estimating the amount of acids combined with an alkaloid in its neutral salts.

Northern Polytechnic Institute, Holloway. — Mr. Thomas Ewan, B.Sc. (Vict.), Ph.D. (Munich), Assistant-Leßurer in Chemistry, The Yorkshire College, Leeds, has been appointed Chief Assistant in the Chemical Department in this Institute.

The method of calibration was as follows:—Each burette and pipette was exactly filled to the zero mark with distilled water, at 15° C. and 10 c.c., delivered into a tared weighing flask and weighed, then the next 10 c.c. were treated in the same manner, and so on until the entire capacity of each was tested. A glass-stoppered cylinder was also standardised. All efforts to standardise a litre flask were thwarted. A large balance sufficiently sensitive to do the work satisfactorily could not be found.

In titration the personal equation plays an important part. Authorities are not agreed on end reaction tints, each operator relying on his own judgment. The writer thinks it correct to titrate to the point where a different colour from the initial colour is developed. In order to obtain standard end reaction tints for alkaloids it will be necessary to prepare some absolutely pure alkaloid; treat a molecular quantity of the alkaloid with an equivalent of the acid in question to form a neutral salt, then add one drop more of the decinormal acid for an acid colour reaction. For alkaline tints add one drop of the centinormal alkaline solution to a solution of neutral alkaloidal salt, theoretically prepared.

In this work the writer titrated from acid to alkaline solutions as follows:—Brazil wood, from yellow to onion-red, the purple ultimately fading to this; cochineal from yellow to bluish red; hæmatoxylin from yellow to brown-orange; litmus from red to onion-red; and methyl orange from red to straw-yellow.

The indicator solutions were prepared according to the most approved processes. Cochineal and litmus were prepared according to the specifications of Sutton's "Volumetric Analysis," sixth edition. Phenolphthalein, 1 grm. dissolved in 1 litre of 50 per cent alcohol. Hæmatoxylin, well crystallised, 1 grm. dissolved in 100 c.c. of strong alcohol. The method best suited for preparing the Brazil wood solution is to place 3 grms. of the wood into a casserole, add 10 c.c. of distilled water, boil gently for a few minutes, cool, and filter. A freshly prepared solution has given the writer the most satisfactory results. Methyl orange, 1 grm. dissolved in 1 litre of distilled water. Considerable difficulty was experienced in obtaining even a fairly satisfactory product of methyl orange. The method proposed by Mr. B. Reinitzer (1894, *Ztschr. Angew. Chem.*, 547, 573; *CHEM. NEWS*, lxx., 225, 239, 249) for preparing the litmus solution did not come to the writer's notice until considerable work had been done with the solution prepared as above.

In titration the following quantities of the several indicators were employed:—Methyl orange, Brazil wood, cochineal, and phenolphthalein, 5 drops each; litmus 10 drops, and hæmatoxylin 3 drops.

The standard solution employed in this investigation, from which the exact strength of the other volumetric solution was determined, was a solution of normal sulphuric acid. This solution was prepared from data obtained by the several methods; titration against pure anhydrous sodium carbonate, using the above indicators; precipitation as barium sulphate and Weinig's (1892, *Ztschr. Angew. Chem.*, 204; *Analyst*, xvii., 99) process. After some experimentation it was found that Weinig's method gave the most satisfactory results. The method is simple, and yields very concordant results. The following are the data obtained from an approximately normal sulphuric acid solution with the above methods:—

Indicators and methods.	No. of c.c. of acid solution required per 10 c.c. of normal sodium carbonate.	Grms. of SO ₃ in 10 c.c. of the solution.
Brazil wood	9'50	0'4211
Hæmatoxylin	9'54	0'4192
Cochineal.. .. .	9'50	0'4211
Litmus	9'50	0'4211
Methyl orange	9'50	0'4211
Phenolphthalein	9'45	0'4216
Weinig's method	—	0'4247
Barium sulphate method	—	0'4200

Due precaution was taken to boil the solution thoroughly with the indicators requiring it. With solutions of the above strength it was impossible to detect any difference in the sensitiveness of most of the indicators.

With the normal sulphuric acid solution a normal solution of pure potassium hydroxide was standardised. From the normal sulphuric acid solution and normal alkaline solution there were prepared, respectively, a decinormal acid solution and a centinormal alkaline solution. The two solutions thus prepared were carefully titrated against each other, employing the above indicators, with the following results:—

Indicators.	No. of c.c. of normal sulphuric acid.	No. of c.c. of centinormal KOH required per 10 c.c. of decinormal H ₂ SO ₄ .	
		LaWall.	Keblcr.
Phenolphthalein	10	101'80	102'00
Brazil wood	10	99'56	100'00
Cochineal	10	100'58	99'80
Hæmatoxylin	10	99'76	100'00
Litmus	10	99'97	99'60
Methyl orange	10	92'67	98'53

My associate, Mr. LaWall, took up a portion of the work, which he executed independently, using, however, the same solutions and apparatus that the writer employed. The above, and all subsequent results, are the average of duplicate, triplicate, or more titrations.

The titration of pure alkaloids, as found in the market, was next undertaken. With quinine and codeine the following method was used:—Two grms. of the alkaloid were placed in the cylinder, dissolved in alcohol, and diluted up to 100 c.c. with alcohol. To 10 c.c. of this solution and the requisite quantity of indicator contained in a suitable beaker, the decinormal acid solution was added to slight excess, agitated, allowed to stand a few minutes, the sides of the beaker well washed down with distilled water, adding about 40 c.c., and the excess of acid titrated back with the centinormal alkaline solution.

With alkaloids not freely soluble in alcohol the following procedure was adopted:—Two grms. of the alkaloid were placed into a 200 c.c. beaker, 75 c.c. of decinormal acid added, the contents of the beaker warmed on a water-bath, and occasionally agitated until the alkaloid was dissolved. The beaker and contents were then cooled, the contents transferred to a 100 c.c. cylinder, the beaker carefully rinsed with several successive portions of water, transferred to the 100 c.c. cylinder, and finally made up to 100 c.c. with water. Each 10 c.c. contained two-tenths of a grm. of alkaloid and 7½ c.c. of decinormal acid solution. After adding the requisite amount of indicator to 10 c.c. of the alkaloidal solution, and diluting up to about 50 c.c., the excess of acid was carefully re-titrated. Two or more titrations were made in every case, with the same solution and indicator, by adding to the solution just finished another portion of the decinormal acid solution, and re-titrating with the centinormal alkaline solution, taking finally the average reading.

The above methods of titration and preparation of solutions were employed with several pure alkaloids. The results are tabulated below.

Indicators.	Quinine.		Strychnine.		Morphine.		Codeine.	
	LaWall.	Keblcr.	Keblcr.	Keblcr.	Keblcr.	Keblcr.	Keblcr.	Keblcr.
Brazil wood.. .. .	99'90	101'97	99'36	98'93	95'75			
Cochineal	105'56	102'54	103'20	99'08	97'09			
Hæmatoxylin	99'81	103'37	100'03	98'17	95'90			
Litmus.. .. .	101'80	103'55	103'54	98'93	96'38			
Methyl orange	—	123'27	104'21	100'59	98'11			

The number of times the analyst is requested to investigate the purity of refined alkaloids is comparatively small, but the crude alkaloids claim a greater share of his time and attention.

(To be continued).

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY CONVERSAZIONE,
JUNE 10TH, 1896.

ALTHOUGH the long expected rain damped everything out-of-doors, there was an exceptionally good attendance at the Soirée of the Royal Society that was held on June 10th.

The exhibits were very numerous and of great interest. Of course, Crookes tubes and Röntgen rays were very much to the front. But real work is now being done in this direction; the mere desire to repeat Dr. Röntgen's experiments is passing away, and some of the first men in science are straining every effort to get more light on this field of research, and probably we shall soon find the disputed points of long or short, transverse or longitudinal waves satisfactorily demonstrated, and thus the way paved for further discoveries.

The very extensive exhibit of Prof. S. P. Thompson, to which we shall refer later on, is a good illustration of this; as was also that of Mr. Herbert Jackson, whose success in the preparation of luminescent screens will greatly help in the study of X rays.

In Room I., The Cambridge Scientific Instrument Company exhibited a Bifilar Pendulum in Action.

Prof. WORTHINGTON, F.R.S., and Mr. R. S. COLE showed a large series of Instantaneous Photographs of Splashes.—These photographs were taken each with an electric spark giving an exposure of less than 3-millionths of a second. The spark could be so timed as to pick out any desired stage of the splash within limits of error not exceeding, as a rule, about 2-thousandths of a second.

Capt. D. WILSON-BARKER, F.R.S.E., exhibited Cloud Photographs taken in different parts of the Ocean World.—Some of these, in particular, were of considerable interest on account of the recent destructive tornado in America.

Prof. W. E. AYRTON, F.R.S., and Mr. T. MATHER exhibited a Small Dynamo for Measuring the Permeability and Hysteresis of Iron.

Mr. J. FRITH showed Different Effects of superimposing a Small Alternating Current on a Direct Current Arc according as Cored Carbons or Solid Carbons are Employed.—This difference was exhibited by the visible motion of the ammeter and voltmeter needles.

In the Council Room, Mr. F. H. WORSLEY-BENISON exhibited a series of Seascape Photographs.—Magnificent specimens of carbon enlargements.

The "Carl Zeiss" Optical Works exhibited their New Portable Binocular Field-glasses and Stereotelescopes.

Dr. JOHN MACINTYRE exhibited a series of Photographs taken by Röntgen Rays that excited very great interest.—(1) Hard tissues. Series of life-size photographs, including bones of head, spine, ribs, extremities, and large joints of body. (2) Soft tissues. Series including neck, tongue, larynx, heart (normal and abnormal), diaphragm, muscles, &c. (3) Animal kingdom. Series of birds, fish, &c. (4) Instantaneous photographs. (Probably got by backing a celluloid film with a fluorescent screen).

The exhibit of Prof. S. P. THOMPSON, F.R.S., to which we have already referred, was very complete, and included—

1. Production by Röntgen's Rays of Electric Dust-shadows.—When Röntgen's rays are allowed to fall upon an electrified sheet of aluminium placed above a plate of ebonite, they carry electric charges to the plate and electrify it. If objects of metal are laid on the ebonite sheet they intercept the Röntgen rays, and the part of the ebonite surface immediately shaded by them does not become electrified. On removing the ebonite plate and

dusting upon it Lichtenberg's powders (mixed sulphur and red lead), the electric shadows become visible.

2. Experiments on Röntgen's Rays.—(a) Cryptoscopic use of luminescent screens (revealing contents of packages, bones of hand, &c.). A large number of new forms of X ray tubes, including one for insertion in mouth, were shown. Also an apparatus of Ebert for producing luminescence by electric oscillations; a stereoscopic X ray photograph of rabbit; and the discharge of electro-scope by Röntgen's rays.

Messrs. SIEMENS BROS. and Co. exhibited Electric Discharges in Vacuum.—Facsimile of Dr. Wm. Watson's vacuum tube of 1751. The first apparatus ever constructed for experiments on the electric discharge in a vacuum. The discharge from a Leyden jar passed through 10 inches, and that from a frictional machine through 3 feet, the whole length of the tube. Facsimile of Lord Cavendish's double barometer of 1751. Used by Dr. Wm. Watson in his researches. Facsimile of Dr. Wm. Morgan's shortened barometer of 1785. Dr. Morgan, by long-continued boiling of the mercury in a barometer tube, produced a vacuum of such excellence that no discharge would pass, and equal therefore to that in a Hittorf or Crookes tube of the present day. It is probable that it would have sufficed for the production of Röntgen rays. Apparatus for showing electric discharges at different degrees of exhaustion, from 70 m.m. to 0 m.m. Photographs obtained by means of Röntgen rays, showing relative transparency of different kinds of wood, minerals, and glass. The apparatus shown has been designed by Dr. Eugen Obach.

Mr. F. E. IVES exhibited the Stereoscopic Photo-chromosome.

Mr. ROBERT L. MOND, M.A., exhibited some of the Apparatus intended for the Davy-Faraday Research Laboratory of the Royal Institution:—

1. Kilogram. automatic balance. (Rueprecht, Vienna).
2. Prism automatic spectro-scope. (Kruss, Hamburg).
3. One-inch spectrometer after Landolt and Brühl. (Hildebrandt, Freiberg).
4. Hüfner photo-spectrometer. (Albrecht, Tübingen).
5. Large polariscope 6-inch Landolt.
6. Small Landolt polariscope. (Schmidt and Haensch).
7. Berthelot platinum bomb. (Golaz, Paris).
8. Glass scale cathetometer. (R. Fuess, Berlin).
9. Petrographical microscope. (R. Fuess, Berlin).
10. Milli-volt meter reading degrees C. for Le Chatelier Thermopile. (Keiser and Schmidt, Berlin).
11. Compensation box of Physikalische Reichsanstalt, Berlin. (Wolff, Berlin).
12. Set of standard resistances. (Wolff).

A more magnificent set of apparatus we doubt if it has ever been the good fortune of any laboratory to possess.

Prof. DEWAR, LL.D., F.R.S., exhibited Portable Apparatus for the production of Liquid Air and Oxygen.

Mr. JOSEPH GOULD gave Demonstrations with his Steel Tuning-bars and Synchronising Sound-generators.

Prof. ROBERTS-AUSTEN, C.B., F.R.S., exhibited Modifications of an Experiment of M. Charles Margot by Professor Roberts-Austen, C.B.—A wire of aluminium is raised, by a current of 30 ampères, to a temperature far above the melting-point of aluminium, but a film of oxide on its surface prevents the wire from breaking. The molten wire through which a current is passing, may then be attracted by a magnet.

Sir DAVID L. SALOMONS, Bart., exhibited a New Form of Spectroscope, with adjustments to vary the width between the lenses.

Mr. T. ANDREWS, F.R.S., showed a number of Photographs taken at high magnifying power of Microscopic Internal Flaws inducing Fracture in Steel Axles, Rails, and Propeller Shafts.

In the Meeting Room, Prof. DEWAR, LL.D., F.R.S., gave a Liquid Air Demonstration, including the following

experiments:—Filtering liquid air; vacuum vessels; boiling at 350 F. degrees below the freezing-point; colour and absorption-spectra; spheroidal state; solid alcohol; frozen soap bubble; distilling mercury and phosphorus; stopping vacuum electric discharge; liquefaction and solidification of gases; fusible metal spring; brittle indiarubber and its expansion by cold; the diamond burning in liquid oxygen; magnetic oxygen; photographic action and phosphorescence; ignition by means of a lens of liquid air; cooling a vessel 380 F. degrees below the freezing-point, until the air of the room condenses on the surface to the liquid state, &c.

PHYSICAL SOCIETY.

Ordinary Meeting, June 12th, 1896.

Captain W. DE W. ABNEY, President, in the Chair.

MR. CAMPBELL read a paper "*On the Measurement of very Large and very Small Alternating Currents.*"

The author advocates the use of air-core transformers, for measuring voltages and currents which are either above or below the range of the instruments available.

If an attempt is made to measure the current in the primary of an air-core transformer by observing the voltage on an open-circuit secondary, it is found that the readings depend on the frequency. In order to overcome this difficulty, the author uses a closed secondary with a very high inductance. In this case the primary current is proportional to the secondary current, which latter may be measured by an ammeter.

The author has also investigated the case of transformers with iron cores, and of which the inductance of the secondary is large. In the case of a ring transformer with a closed magnetic circuit, if the load on the secondary consists solely of a Kelvin 100-ampere balance of very low resistance, the ratio between the primary and secondary currents is practically constant. With an open magnetic circuit transformer, however, this is not found to be so, as the ratio between the primary and secondary currents varies considerably with the frequency.

MR. BLAKESLEY said that the author's arrangement could only be used for measuring the current in the primary. He (Mr. Blakesley) had shown how to measure alternating currents by means of dynamometers, and without the necessity for any special apparatus.

MR. GRIFFITHS exhibited and described his Improved Form of Resistance Box.

This resistance box has many novel features:—

(1). It permits of all the coils being compared with one another, without the use of standard coils and with great ease and rapidity. Hence it is sufficient at any time to compare any one of the coils with a standard to obtain the correction to be applied to all the coils. (2). The bridge wire can be calibrated by means of the box itself. (3). The temperature of the coils can be accurately determined, since they consist of bare platinum-silver wire, wound on mica and immersed in an oil bath, which bath is kept stirred. (4). The resistance of the leads from the box to the object being tested is eliminated, as well as any error due to a change in this resistance with temperature. (5). The coils are arranged according to a binary scale, and the author claims that it is possible to measure resistances up to 105 ohms to within 0.000001 ohm. (6). All the coils, after being adjusted, have been heated to redness and allowed to cool slowly, so that all strain has been removed from the wire. (7). By having a separate pair of blocks for each plug, it is impossible for the insertion of one plug to affect the fit of a neighbouring plug. The plugs themselves are so made that no part of the plug is wider than the top of the hole, and so it is impossible to wear "a shoulder" on the plug.

Prof. A. GRAY said that Mr. Griffiths had discovered and remedied all the weak points of the ordinary form of bridge. Lord Kelvin had ordered the paraffin to be melted off the coils of one of his resistance boxes, and it was found that the resistance of the coils altered considerably, owing, no doubt, to the strain to which the wire had been subjected when embedded in the solid paraffin. Lord Kelvin had made coils without paraffin, and was specially in favour of the use of the binary scale.

Prof. S. P. THOMPSON said he considered the binary scale the weak point of the author's arrangement, since it did not permit of ratios other than 1 to 1 being employed.

MR. CAMPBELL asked what current could be safely passed through the coils.

The author, in his reply, said that he believed it to be a great mistake to employ any ratio for the arms other than 1 to 1.

Prof. S. P. THOMPSON read a communication on "*Röntgen Rays.*"

The author, after describing the various forms of tubes he had made with a view of discovering the best form for the production of Röntgen rays, gave an account of the experiments he had made to try and obtain some indication of polarisation. In this connection a large number of crystals had been tested, but the experiments have all given negative results.

The author exhibited an electroscope with aluminium leaves, and enclosed in a wire gauze screen to protect it from the influence of outside electric changes, by means of which he was able to show the discharge of a positively or negatively electrified body by means of the X rays.

A method of obtaining dust figures by the discharge of an electrified body by the X rays was shown, and some of the results which have been obtained were exhibited.

All attempts to obtain true reflection have failed, although it appears as if most bodies, including air, were capable of giving diffuse reflection.

DR. SHETTL, who was announced to give a paper on Röntgen rays, explained that he had just discovered that the effects he had intended to describe were due to red light which had penetrated his dark room.

Prof. DU BOIS said that Galitzine had found that Röntgen rays were polarised by tourmaline, a special form of developer being employed. The behaviour of tourmaline to light waves presents some curious features; for if the wave-length is increased, a point is at length reached where the ordinary and extraordinary rays are equally absorbed. For greater wave-lengths the ordinary conditions are reversed. If the Röntgen rays are not homogeneous, the contradictory results obtained by different observers might be due to the fact that they were working with rays which were differently absorbed by tourmaline.

MR. SWINTON said he had tried the effect of heating the kathode, and had obtained results similar to those which were obtained by the author. Mr. Swinton further said that he had found that the blue luminescence sometimes observed depended on the size of the kathode. With tubes in which the kathode was almost a complete hemisphere, it was impossible to eliminate this blue luminescence.

MR. APPEYARD suggested the performance of the experiments under the surface of a dielectric.

Prof. GRAY said he had obtained some indication of regular reflection, but nothing definite.

The author, in his reply, said that it had been found that if the Röntgen rays are reflected from a surface of sodium *in vacuo* the amount reflected is a minimum for normal incidence, and increases at oblique incidence. Comparing this behaviour with that of ultra-violet light, it supports the idea that the Röntgen rays consist of transverse vibrations.

The Society then adjourned till June 26th.

CHEMICAL SOCIETY.

Extra Meeting, May 28th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

PROFESSOR P. PHILLIPS BEDSON, M.A., D.Sc., delivered the Lothar Meyer Memorial Lecture.

After relating the more important events in the career of Lothar Meyer, his experimental work on the "Gases of the Blood" was considered, the results of which form the basis of the teaching at the present day. The history of Meyer's independent contribution to the "Periodic Law" was examined, and the development of this system of classification of the elements was traced in Meyer's writings from 1864 to the close of 1869, when he published the paper containing the well known curve of atomic weights and atomic volumes. The investigations of Meyer, undertaken with the object of promoting the systematic arrangement of inorganic chemistry, were noticed. The utilisation of Graham's determination of the rates of transpiration of gases to deduce from them the molecular volumes of gases was next considered, and a description given of the investigations by which it was sought to determine the rates of transpiration of vapours, and thus to arrive at the molecular volumes of vapours. In tracing the history of Meyer's literary work, more especially of the "Modernen Theorien," first published in 1864, of which he was preparing a sixth edition at the time of his death, it was pointed out how great had been Meyer's influence on the promotion and advancement of chemical theory during the past thirty years.

Sir HENRY ROSCOE proposed, and Dr. GLADSTONE seconded, a vote of thanks to Professor Bedson, which was supported by Dr. RUSSELL, and carried unanimously.

Ordinary Meeting, June 4th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

Mr. J. C. Stead was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Walter William Cobb, Hilton House, Atherstone; Arthur Edwin Saville, 33, Richmond Terrace, Darwen; Kotaro Shimomura, Dolemachi, Kioto, Japan; John James Whimster, 12, Rutland Terrace, Stockton-on-Tees; Alfred James Wilcox, The Grammar School, Guisborough, Yorks.

The PRESIDENT announced that the following Address was to be presented to Professor Cannizzaro, a Foreign Member of the Society, on the occasion of his seventieth birthday, in July next.

"ADDRESS TO PROFESSOR CANNIZZARO.

"On behalf of the Council and Fellows of the Chemical Society of London, we, the President and Officers, beg to offer you, Stanislas Cannizzaro, our most sincere congratulations on the attainment of your seventieth birthday. A society such as ours, having for its object the promotion of chemical science, cannot but acknowledge that your association with us as Foreign Member since 1862, and in 1872 as our Faraday Lecturer, is a source of the greatest satisfaction to all our Fellows, and we desire, in giving expression to this sentiment, to convey to you the wish that your name may for many years continue to add lustre to the roll of our membership.

"At a critical period in the history of our science, when the conceptions of equivalence, atomic weight, atoms, and molecules were ill-defined, and when much confusion existed concerning the fundamental doctrines of chemical theory, you were the first who succeeded in directing the attention of chemists in general to the law which will ever be associated with the name of your illustrious countryman Amadeo Avogadro. Not only did you make

known the importance of this law in its chemical bearings, but with the clearest perception of its far-reaching consequences, you demonstrated in your masterly memoir, 'Sunto di un corso di Filosofia Chimica,' published in 1858, how by its adoption the conflicting views of many of the most eminent chemists of that period could be reconciled and made harmonious. By your advocacy the law of the specific heats of the elements, enunciated by Dulong and Petit in 1819, became more firmly established as an essential principle of chemistry. Our modern methods of determining molecular weight by means of vapour density, and the interpretation of abnormal vapour densities in the light of the theory of dissociation are the direct outcome of your labours on behalf of chemical science. The revised system of the atomic weights of the elements, which has rendered possible their rational classification in accordance with the periodic law of Newlands, Mendeleeff, and Lothar Meyer, and which was necessitated by the acceptance of the hypothesis of Avogadro, has now become universally recognised.

"As one of the founders of the new chemistry, your name will live in the annals of our science as that of a man held in the highest honour and esteem—a name worthy of being joined with those of your great countrymen, Galileo, Torricelli, Volta, and Galvani.

"The congratulations which we now offer you in the name of our Society express the unanimous feeling of the chemists of this country, and not least of ourselves, the officers of the Chemical Society, who are entrusted with the honour of conveying them to you."

The following Address was presented to Lord Kelvin on the occasion of the completion of his fiftieth year as Professor of Natural Philosophy in the University of Glasgow.

"ADDRESS TO THE RIGHT HON. THE LORD KELVIN, D.C.L., LL.D., F.R.S., FROM THE CHEMICAL SOCIETY OF LONDON.

"THE Council of the Chemical Society of London desire to convey to you their sincere congratulations on the occasion of the Jubilee of your Professorship of Natural Philosophy in the University of Glasgow.

"THE period during which you have occupied this Chair has been distinguished by the rapid growth of our knowledge of Nature, and the applications of this knowledge to the public good.

"IN the past, great names in England and in other countries have been associated with important theoretical advances, and with technical inventions; but it has been given to few, and to none so much as to yourself, to combine a powerful grasp of the most recondite questions in Science with the ability to apply knowledge in an eminently successful manner to the service of mankind.

"WITH the growing perception of the dependence of one department of Science upon another, we, as Chemists, feel more and more the far-reaching applications of your contributions to Physics, and it is with gratitude and pride in your work that we to-day join with representatives of other Sciences and other nations in offering homage to one whose name will ever occupy a foremost place among the pioneers of Natural Knowledge."

(To be continued).

Physiological Study of Persian Cyclamens.—Alex. Hébert and G. Truffaut.—The methods habitually employed for cultivation on the large scale are not always suitable for the production of flowers. If the distribution of fertilising matters always occasions an abundant production of vegetable matter, this action may fall upon the leaves and not upon the flowers.—*Comptes Rendus*, cxvii., No. 21.

NOTICES OF BOOKS.

Explosives Act, 1875 (38 Vict., c. 17). *Twentieth Annual Report of Her Majesty's Inspectors of Explosives*; being their Annual Report for the Year 1895. London: Printed for Her Majesty's Stationery Office by Eyre and Spottiswoode. 1896.

THE Inspectors of Explosives, in pursuing their necessary supervision, have not had to chronicle any great calamity, whether due to carelessness or to malice. The outcry raised at the first passing of the Act (1875), that the regulations imposed might fetter competition with alien manufactories, have died away in view of the fact that foreign countries—notably Belgium, France, and Germany—have introduced laws and regulations based to a great extent upon our own, but much more stringent.

The number of deaths from explosions during the year has been ten, a figure above the average during the last ten years, but due not so much to any falling off in the high standard reached in the manufactories, or to negligence on the part of the inspectors as to the increase in the number of factories and in the number of hands employed.

The total number of factories under continuing certificate and license is now 134 (not including "small firework" and "toy firework" factories). This is an increase of four on the previous year. No factories have become extinct.

The four new factories are:—No. 165, for cordite, gun-cotton, and collodion-cotton; No. 166, for Rosslyn smokeless powder No. 1, gun-cotton, and collodion-cotton; and No. 167 and 168, for collodion-cotton.

The following have been added to the list of authorised explosives:—Dahmenite A, elecronite Nos 1 and 2, emerald powder, Faversham powder, Pigou's military smokeless powder, Pigou's sporting smokeless powder, roburite No. 3, Rosslyn smokeless powder No. 1, Rosslyn blattite, low tension electric fuzes (No. 5 definition), low tension electric detonator fuzes for ditto.

The limit of quantity of gunpowder, or of ingredients to be made into gunpowder, to be ground under any single pair of mill stones, &c., has been extended to 100 lbs.

Quick-firing ammunition, which was formerly licensed only for direct issue to Her Majesty's land and sea forces, may now be made for export (if water transport only) in the case of one factory on the bank of the Thames. The inspectors have paid 186 visits to the factories, and consider that, as a whole, the factories for explosives in the United Kingdom will compare extremely favourably with any other factories at home or abroad.

The institution of proceedings has been necessary in four cases only.

Some boys broke into a factory near Birmingham, and stole some coloured stars which afterwards exploded, killing one boy. Two cases of illegal manufacture of fireworks have been detected; in one of these a boy was fatally injured.

The list of outrages and attempts at outrage by means of explosives, from 1881 to 1895 inclusive, looks sufficiently gloomy. In those cases where the conviction of the offenders was obtained, the sentences passed were too low. It is a remarkable inconsistency that, whilst there is an outcry against the sale of poisons, no demand is raised for stringent regulation of the common sale of explosives and ammunition, the lawful uses of which are so much more rare and the possible injuries so much greater.

A case against the New Explosives Company, of Stowmarket, for the improper labelling of an explosive, is still pending.

In connection with the question of infernal machines and bombs, it appears that such devices may be safely examined by means of the X rays.

Among Government accidents mention is made of an explosion on board of the War Department powder-barge *Petrel*. The barge ran aground at Hope Point, and the master was drowned. No definite conclusion could be reached as to the cause of the disaster, which is the more unsatisfactory as the vessel was fitted out in exact conformity with the regulation for the carriage of explosives.

On April 22nd an explosion took place at Waltham Abbey in connection with the manufacture of cordite, in which two persons were slightly injured.

An accident occurred during the trial of a Maxim gun, with injury to two persons. The inspectors give a strong caution concerning unexploded charges, or portions of charges, left lying about after gunnery practice or experiments with explosives. This has been the cause of twelve deaths, and of twelve cases of injuries which did not prove fatal. It is recommended that wooden tools should be used in searching for or removing any *débris* from such operations.

A serious dynamite explosion took place on Nov. 28th at the Leeuwfontein factory. It is supposed that 50,000 lbs. of dynamite were exploded with widespread damage, but, as the establishment was not working at the time, none of the 800 hands were injured.

The explosions in America have been numerous and serious. On January 15th an explosion ensued at Butte, Montana, resulting in the death of from 75 to 100 persons and injuries to not fewer than 150. It was supposed to be the work of an incendiary, but the perpetrator could not be detected. The explosives were giant powder and gunpowder. On May 21st fourteen persons were killed at Pinola, California, by the spontaneous ignition of impure nitro-glycerin.

At Partenbury, West Virginia, a boat loaded with 250 cans of nitro-glycerin exploded, killing or injuring about 200 persons, and wrecking houses and other property in the neighbourhood.

At Takao, in Formosa, the magazine of one of the forts blew up, and 2000 Chinese soldiers were killed (?).

Two explosions are recorded in India,—one on March 27th in the Kolar gold-field, and the other on April 4th at the Bangalore gold-mine. In each case sixteen persons were killed. The former accident was due to an attempt to steal blasting gelatin, and the latter to the careless handling of detonators.

In Palma, in Majorca, a serious explosion took place on November 21st, killing 92 persons and seriously injuring some others.

A curious accident took place in London on September 21st. A stockbroker, leaving his private office hastily to speak to a client, bumped up against a counter in the outer room. A hissing sound was heard, and his coat was seen to be on fire. It appears that he had some chlorate of potash lozenges loose in his pocket, and at the same time a safety-match box. In bumping against the counter, the lozenges came briskly in contact with the igniting surface of the match-box and occasioned the accident.

Three cases of suicide scarcely deserve particular notice.

Scares and hoaxes have become scarce since two men were fined £48 each for sending bogus bombs to a number of prominent characters.

Explosives intended to produce serious damage, either from motives of private malice or from political feeling, have been numerous. The most serious was that at Tulce, in Russia, where the artillery barracks were blown up and about 300 officers and soldiers killed. It was supposed to be a Nihilist plot.

Two anarchists were engaged in manufacturing a bomb at Ancona, when it burst and seriously injured them both.

No right-minded person, after duly considering this report, free as it is of anything of an alarmist character, can fail to perceive what a power for evil has been placed in the hands of the criminal classes by the invention of

the "high" explosives, and that their common sale requires to be placed under more stringent regulations.

Book of Tables of Chemico-Organic Compounds: a Work of Reference for Chemists, Apothecaries, Physicians, &c. ("Tabellenbuch der Organisch Chemischen Verbindungen. Ein Hilps und Nachschlagebuch für Chemiker, Apothiker, Aerzte, &c.") By Dr. Fr. POLLAK. Karlsruhe: Memnich. 1896.

In this most valuable book we find in parallel columns the name of each compound, its formula, the equation showing its origin or preparation, its melting-point, boiling point, crystalline form and colour, its solubility in water, in alcohol, ether, exceptionally in other organic fluids, and the literature of the substance shown by reference to the abbreviated titles of the principal scientific journals of all countries, and the transactions of the leading scientific societies.

To students, investigators, and manufacturers engaged in the ever-widening field of organic chemistry, this book will prove simply inestimable.

The Old Light and the New. By W. M. ACKROYD, F.I.C. London: Chapman and Hall. Pp. 102.

FROM the outside appearance of this book we expected a mass of information on the discoveries of Dr. Röntgen and others, and we were somewhat disappointed to find the bulk of the space occupied by the theory of colours, &c. The little that there is about the so-called "new light" is meagre, and consists chiefly in the tabulation of some of the more important communications of the various societies in England upon this subject,—valuable indeed in its way, but not exactly what we expected to find. Still we hope it will have a wide distribution, for what little information it does give has the advantage of being clear and concise. Exception must be taken to the position of the X rays in the spectrum diagram on p. 11. Having little or no refrangibility, their place would not be beyond the ultra-violet rays, but they should form a continuation in practically a straight line with the incident white light.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 21, May 25, 1896.

Source and Nature of the Potential directly Utilised in Muscular Work according to the Respiratory Exchanges in a Man in a State of Inanition.—A. CHAUVÉAU.—The author's conclusions are:—According to the evidence supplied by the respiratory exchanges, fat never constitutes the potential directly utilised by the muscles when working in man in a state of abstinence. It is in the form of carbohydrates that this energetic potential is supplied to muscular activity. The work of the muscles tends to exhaust the reserves of glycogen and of glucose when this potential is accumulated. But these reserves, in spite of abstinence, tend to reconstitute themselves in proportion to their consumption.

Immediate Destination of Fatty Foods.—A. CHAUVÉAU, with the collaboration of MM. TISSOT and DE VARIGNY.—As for the immediate destination of alimentary fats, it can be nothing other than the maintenance of the provisions of potential of the organism, whether the reserves of carbohydrates, if these are impoverished

at the moment when digestive absorption has rendered the alimentary fat utilisable, or the reservoirs of adipose tissue where the fatty principles are stored up.

Determination of the Deviation of the X Rays by a Prism.—MM. HURION and IZARN.—The use of two vertical slits situate at some centimetres, the one behind the other, the former of which is illuminated by a source of light of great apparent diameter, furnishes a sort of luminous plane, the upper half of which can be made to pass through a prism.

Refraction of the X Rays.—M. GOUY.—The refraction of the X rays, if it exists, is inferior to two seconds, whence the index cannot differ from unity by more than $1/200,000$. These experiments—with others which the author intends to describe—show the total absence of diffraction.

Action of Gaseous Hydriodic Acid and of Phosphonium Iodide upon Thiophosphonyl Chloride.—A. BESSON.—Hydriodic acid dissolves simply in thiophosphonyl chloride, PSCl_3 , if we operate in a refrigerating mixture of ice and salt, but a reaction sets in if the temperature of the mixture rises slightly. At the temperature of melting ice the liquid blackens, and hydrochloric acid and hydrogen sulphide are given off. Iodosulphide, P_2SI_2 , is an orange-coloured solid melting at 75° . It is very soluble in carbon disulphide. Ouvrard's phosphorus iodosulphide is yellow, fusible at 106° , and has the composition $\text{P}_4\text{S}_3\text{I}_2$.

Hydration of Pinacoline.—MAURICE DELACRE.—This paper is not adapted for useful abstraction.

New Method of Preparing Glyceric Acid.—P. CAZENEUVE.—Glycerin, in presence of soda and silver chloride, gives, if heated, glyceric acid, with the simultaneous production of metallic silver and sodium chloride.

Action of Ethyloxalyl Chloride upon Aromatic Hydrocarbons in presence of Aluminium Chloride.—L. BOUVEAULT.

New Derivatives of Cyanacetic Ethers.—M. GUINCHANT.—These two papers are adapted neither for abridgment nor for insertion in full.

A New Oxidase, or Oxidising Soluble Ferment of Vegetable Origin.—G. BERTRAND.—Laccase is not the only soluble oxidising ferment which exists in plants, but may be regarded as the type of a series of analogous substances.

Zeitschrift für Analytische Chemie.
Vol. xxxiv., Part 6.

Determination of Urea.—B. SCHÖNDORFF, PFLÜGER, and BLEIBTREU.

Detection of Pentoses in Urine.—SALKOWSKI and JASTROWITZ.—The new sugar observed by these authors in human urine is found to be a pentose.

Poisonous Action of Zinciferous Water on Fish.—ED. v. RAUMER (*Forschungs-berichte über Lebensmittel*).—Zinc sulphate, even in very minute quantities, exerts a highly deleterious action upon fishes.

Toxic Action of Different Alcohols on Plants and the Lowest Animals.—M. TSUKANOTO (*Forschungs-berichte über Lebensmittel*).—The toxic action of the saturated alcohols on organisms of different kinds rises with the molecular weight. Isomeric alcohols have not an equally intense action. Allyl alcohol is much more poisonous than the saturated alcohols.

Re-calculation of the Atomic Weights.—J. THOMSEN (*Zeit. Physik. Chemie*).—The author's calculations are based upon the experiments of STAS. The atomic weight of hydrogen appears as 0.9992.

Atomic Weight of Tellurium.—B. BRAUNER.—From the CHEMICAL NEWS.

MEETINGS FOR THE WEEK.

TUESDAY, 23rd.—Photographic, 8.

WEDNESDAY, 24th.—British Astronomical,
Society of Arts, 4. (Anniversary).
Geological, 8.

THURSDAY, 25th.—Royal Society Club, 6.30. (Anniversary).

FRIDAY, 26th.—Physical, 5. "Admittance and Impedance," by F. Bedell. "Properties of a Body of Negative Resistance," by S. P. Thompson. "On Bare Wire Resistances," by H. F. Burstall.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1909.

EMISSION OF NEW RADIATIONS BY METALLIC URANIUM.

By HENRI BECQUEREL.

I HAVE shown, some months ago, that the salts of uranium emit radiations the existence of which had not as yet been recognised, and that these radiations possess remarkable properties, some of which may be compared to the properties of the radiation studied by Prof. Röntgen. The radiations of the uranium salts are emitted not only when the substances are exposed to light, but even when they have been kept in darkness, and for more than two months the same fragments of various salts kept secluded from any known exciting radiation have continued to emit new radiations almost without any appreciable decrease. From March 3rd to May 3rd the substances were shut up in an opaque box of cardboard. Since May 3rd they have been placed in a double box of lead, which remained in the dark chamber. A very simple arrangement permitted me to slip a photographic plate below a black paper extended parallel to the bottom of the box, and on it lay the substances in question without these being exposed to any radiation not traversing the lead. Under these conditions the substances studied continue to emit active radiations.

If we expose to the sun, or preferably to the electric arc or to the spark from the discharge of a Leyden jar, a fragment of one of the salts kept in the dark, we communicate to it a slight excitement to the emission of the radiations which we are studying; but this excitement declines in a few hours, and the substance resumes the state of a slow decrease.

I have likewise shown that these radiations are reflected and refracted like light; they decompose the silver salts of a photographic plate and the silver iodide deposited on a Daguerre plate.

They discharge electrified bodies and traverse substances opaque to light, such as cardboard, aluminium, copper, and platinum.

The weakening of these radiations, through the screens which we have just mentioned, is smaller than the weakening of the radiation emanating from the anticathodic wall of a Crookes tube through the same screens.

All the uranium salts which I have studied, whether phosphorescent to light or not, and whether crystalline, melted, or dissolved, have given me comparable results. I have therefore been led to think that the effect was due to the presence of the element uranium in these salts, and that the metal would give effects more intense than its compounds.

The experiment made some weeks ago with commercial powder of uranium which had been kept for a long time in my laboratory confirmed this prevision; the photographic effect is notably stronger than that produced by one of the salts of uranium, and by uranium-potassium sulphate.

Before publishing this result I resolved to wait until our colleague, M. Moissan, whose beautiful researches on uranium are published this day, could place at my disposal some of his recent products. The results have been still more distinct; and the impressions obtained on a photographic plate through black paper with crystalline uranium, cast uranium, and uranium carbide have been much more intense than with the double sulphate used as a check on the same plate.

The same difference has been observed in the phenomenon of the discharge of electrified bodies. Metallic uranium

occasions the dissipation of the charge much more rapidly than do its salts. The following figures relating to the action of a disc of cast uranium, obligingly lent me by M. Moissan, gives an idea of the order of magnitude of this increase.

In a first series of measurement the disc of cast uranium was placed below the gold leaves of a Hurmuzescu electroscope, and very near them. For the initial charges corresponding to 20° deviation of the gold leaves, the speed of approximation expressed in seconds of an angle in one second of time has been as a mean 486. A disc of cardboard, the surface of which was sensibly equal to that of the disc of uranium, was then taken, arranging on it flat fragments of the double sulphate above mentioned, and this disc was then substituted for the disc of uranium. Under these conditions the discharge did not take place regularly, the curve of the deviations of the gold leaves as a function of the time was no longer a right line, and the mean speed of dissipation of charges equal to the foregoing varied from 106.2 to 137.1, according to the disposition and the form of the gold leaves. The ratio of the speeds corresponding to uranium and to the double sulphate has varied therefore between 4.56 and 3.54.

A better disposition consists in placing the substances outside the electroscope above the copper ball of the stem, substituting for the cap of the apparatus a metallic cylinder closed by a flat metal plate perforated with a suitable aperture. We thus obtain discharges very sensibly proportionate to the times and the velocities of loss, for the charges deflecting the gold leaves of 10° have been 78.75 for uranium and 21.53 for the double-uranium potassium sulphate. The relation of the two numbers is 3.65.

Whilst continuing the study of the novel phenomena, I have thought it not uninteresting to signalise the emission produced by the uranium, which is, I believe, the first instance of a metal presenting a phenomenon of the order of invisible phosphorescence.—*Comptes Rendus*, cxxii., p. 1086.

IDENTIFICATION AND SEPARATION OF THE PRINCIPAL ACIDS CONTAINED IN PLANTS.

By L. LINDOT.

THE reactions which enable us to distinguish the vegetable acids are not numerous, and often uncertain in their application; and if we can characterise tartaric acid,—thanks to the insolubility of its potassium salt in the mixture of alcohol and ether,—we are more embarrassed if it is requisite to isolate the other acids, and especially the citric and malic, so frequently present in vegetable tissues.

When studying the compounds of these acids with quinine and cinchonine, I have found that the resulting salts, and especially the acid salts, present differences of solubility in methylic alcohol, such that it is easy to distinguish citric and malic acids and to separate them from vegetable juices.

1. Cold methylic alcohol at 95° Gay-Lussac dissolves only 0.3 per cent of acid quinine citrate; so that if we add quinine to a methylic solution of citric acid, at 2 or 2.5 per cent, this alkaloid is dissolved at first, giving then rise on stirring to a bulky crystalline precipitate of acid citrate, which may extend to 9.3 per cent of the theoretical quantity. An excess of quinine, with reference to the composition of the acid salt, re-dissolves the precipitate, and then ultimately the neutral citrate crystallises; its solubility is greater than that of the acid citrate, and rises to 3.3 per cent.

Under identical conditions the acid quinine malate (solubility in cold methylic alcohol at 95° Gay-Lussac, 8.2 per cent) and the neutral malate (solubility 8.0) remain in solution. The presence of malic acid slightly

interferes with the precipitation of acid quinine citrate, and when in a mixture of the two acids the quantity of malic acid represents 25, 50, 100, or 200 per cent of the quantity of citric acid, the weight of the acid quinine citrate obtained is not more than 99, 97, 94, or 89 per cent of the citrate which would be obtained in a liquid free from malic acid.

Under the same conditions the acid quinine oxalate (solubility 9.2 per cent) and the neutral oxalate (solubility 8.2 per cent) remain equally in solution; but the oxalic acid increases the solubility of quinine citrate in larger proportions than does malic acid.

The precipitate of quinine citrate may be confounded with the quinine acid tartrate (solubility 2.4 per cent) and the acid succinate (solubility 1.2 per cent).

II. Cinchonine dissolved in methylic alcohol precipitates malic acid under conditions identical to those in which quinine precipitates citric acid. However, the solubility of acid cinchonine oxalate in methylic alcohol at 95° Gay-Lussac and in the cold, which is 2.5 per cent, is higher than that of quinine citrate; but the other salts of cinchonine are so soluble that the precipitation above mentioned may be considered as characteristic of malic acid. Acid cinchonine tartrate is, in fact, soluble at 20.6 per cent; the acid nitrate, the acid oxalate, and the acid succinate do not crystallise until their solutions have been brought to the state of syrup. The tartaric, citric, oxalic, and succinic acids, if mixed with malic acid, increase in a striking manner the solubility of cinchonine malate in methylic alcohol; it is thus that citric acid, added to malic acid in the proportions of 20, 50, 100 per cent, hinders the tenth, the half, and even the whole of the oxalic acid from crystallising as a cinchonine salt.

III. To apply the foregoing reactions to the extraction of the acids of a vegetable juice, it must first be evaporated in vacuum, and re-dissolved in methylic alcohol as concentrated as possible. If the juice contains potassium bitartrate and free tartaric acid, it must be treated with alcohol and ether to separate the tartar, and precipitate the tartaric acid in the state of bitartrate by a limited addition of potassa to the same ethero-alcoholic liquor. To eliminate the excess of potassa, we precipitate all the acids by basic lead acetate, and liberate them again with hydrogen sulphide. It is proper to operate in the same manner if the juices contain an excessive quantity of sugars or foreign matters.

The concentrated acids being dissolved in methylic alcohol, we take a known volume of the liquid, which we dilute with methylic alcohol, so that the solution may contain 2.5 per cent of acid, and we add to the liquid increasing quantities of quinine in powder, until after being stirred for some time it sets into a crystalline mass. The quantity of quinine added should not exceed 160 to 170 parts to 100 parts of the citric acid supposed to be present. We must, in fact, avoid adding an excess of quinine, which would dissolve—momentarily at least—the acid citrate, and form neutral citrate, which is more soluble. When the proportion of quinine which must be added has thus been determined, we treat the residue of the liquid with the calculated quantity of quinine. After settling for twenty-four hours we filter, and re-commence the same operation upon the mother-liquor.

If the liquid does not precipitate under these conditions,—that is to say, if it contains no citric acid,—we search for malic acid, by adding in 1 part of the methylic liquid, as concentrated as possible, increasing quantities of cinchonine, the maximum dose of which may be fixed at 140 to 150 per cent of the estimated quantity of malic acid.

If the two acids are simultaneously present, when the liquid is no longer precipitated by quinine we add cinchonine, the action of which is not interfered with by the excess of quinine.

It is easy to recover the corresponding acids from the salts of quinine and cinchonine obtained. It is sufficient to add to the aqueous solution of these salts ammonia, to filter off the alkaloids, to precipitate the liquid with

basic lead acetate, and then decompose the precipitate with hydrogen sulphide. Or we may render both the acid and the base insoluble by means of baryta, exhaust the dried precipitate with alcohol, and decompose the barium salt with sulphuric acid.

By these methods I have been able to extract the citric acid contained in lemons and gooseberries, and extract the malic acid contained in cherries.—*Comptes Rendus*, cxvii., p. 1185.

PREPARATION AND PROPERTIES OF URANIUM.

By HENRI MOISSAN.

In a paper published on February 20th, 1893, we have established that uranium oxide, hitherto regarded as not reducible by carbon, can yield metallic uranium in presence of this substance at the high temperature of my electric furnace. We have since demonstrated the existence of a definite crystalline compound of uranium and carbon, C_3U_2 .

We shall now give a more complete study of this metal.

It is known that metallic uranium was first prepared by Peligot by reducing uranium chloride with potassium in a platinum crucible. By this procedure we obtain a grey powder, in the midst of which are found some small metallic globules.

Different chemists have slightly modified this operation, and in 1886 Zimmermann resumed the study of uranium, and obtained the metal by reducing uranium chloride with sodium. The isolated metallic globules in this preparation were few in number. Their fusion was due to the intense heat developed by the action of the alkaline metal upon the chloride.

We have repeated all these experiments. If we operate in a platinum crucible, the uranium is always soiled with this metal. In Zimmermann's preparation the uranium always contains 2 per cent of iron and a small quantity of sodium.

Moreover, whatever is the method employed, all these uranums in powder contain nitrogen and often oxygen. As we shall demonstrate below, metallic uranium has a strong affinity for gaseous nitrogen, hitherto unknown.

We thought that this action of the alkaline metals might be more advantageously employed by means of a double compound of sodium and uranium.

Preparation of the Double Uranium and Sodium Chloride, $UCl_4 \cdot 2NaCl$.—When we pass a current of vapour of uranium chloride over sodium chloride we obtain a double chloride, which on cooling congeals to a crystalline mass of an apple-green colour, melting at 390°, fusible about 390°, soluble in cold water, and dissociated by alcohol.

This preparation is very easily made in a tube of Bohemian glass, forming at one end uranium chloride by the action of chlorine upon uranium carbide, and causing this chloride to pass over fragments of sodium chloride placed at the other end and heated to dull redness. The solid alkaline chloride begins to be coloured, seizing all the vapour of uranium chloride, and then the mass melts rapidly.

We know that uranium chloride, UCl_4 , is greedy of moisture, fumes in the air, and is not easily manageable. On the contrary, the crystalline double chloride is much less hygroscopic and more stable. If fused, it yields a very stable liquid, which does not apparently give off vapours.

Reduction of this Double Chloride by Alkaline Metals.—The reduction has been effected in a very thick iron cylinder, closed with a screw stopper. It is charged with alternate layers of 300 grms. double chloride and 100 grms. sodium recently cut.

The apparatus being closed, it is placed in a very brisk wood fire, when it is heated for twenty-five minutes. The heat disengaged by the reaction is so intense as to raise the block of iron to a cherry-red heat in a few instants. When cold, the cylinder is opened, and the powdery contents treated at first with alcohol at 96° to remove the excess of sodium, then rapidly washed with water which has been boiled and allowed to cool, then exhausted with alcohol and lastly with ether.

Preparation of Uranium in the Electric Furnace.—We have indicated in a former paper on uranium carbide how the industrial uranium carbide must be purified. The uranium having been brought to the state of green oxide (U_3O_8), is intimately mixed with sugar charcoal in fine powder in the following proportions:—

Uranium oxide	500 grms.
Sugar charcoal	40 "

About 500 grms. of this mixture are placed in a coke crucible and submitted in the electric furnace for seven to eight minutes to a current of 800 amperes and 45 volts. We thus obtain a fused ingot of about 350 grms. The metal thus prepared, if the heating has been well conducted, contains very little carbon, and sometimes even not a trace. On the contrary, we may find in it a small quantity of oxide, which then furnishes a "burnt metal," the physical properties of which are notably modified. If the duration of the heat is too long, the metal is readily carbed, and we obtain a cast metal and then a crystallised carbide, C_3U_2 . To avoid the action of nitrogen, it is better to make these experiments in a tube of coke closed at one end, and adopting the arrangement above indicated.

Refining Uranium at the Forge.—When we prepare by the above procedure an uranium containing from 0.1 to 0.5 of carbon, we may refine the exterior of the fragments by heating them for some hours in a crucible lined with green uranium oxide. To realise this experiment we must place the crucible containing the uranium oxide and the metal in the middle of another crucible filled with titaniferous carbon finely pulverised. The neglect of this precaution might produce a yellow metal coated with nitride.

Preparation of Metallic Uranium by Electrolysis.—The double uranium chloride above described is electrolysed with the greatest ease. It yields at the negative pole a sponge of uranium containing frequently small crystals of this metal. To have regular working it is sufficient to have at the terminals a difference of potential of 8 to 10 volts. We have generally used a current of the density of 50 amperes. The bath is kept in fusion by the thermic action of the current itself.

The electrolysis is effected by means of electrodes of pure charcoal, and the chloride is placed in a cylindrical vessel of porcelain. This vessel is closed by means of a plate of porcelain, giving passage to the two electrodes and to a glass tube bent at a right angle. This tube enables us to introduce above the melted salt a current of hydrogen very dry and very free from nitrogen.

After complete cooling, the contents of the crucible are taken up with ice-water, and washed rapidly with alcohol; for uranium, if finely divided, decomposes water at the ordinary temperature.

This uranium is crystalline, and certain parts near the electrode appear even in crystals measuring 1 m.m. on the sides.

If we employ an iron electrode, we obtain alloys of iron and uranium of a silvery white, which may be easily filed and which have a very fine grain.

Physical Properties.—When uranium is very pure its colour is absolutely white, less bluish than that of iron, though it takes a similar polish. If the metal has a yellow tint, we may always suspect the presence of nitrogen. To its specific gravity we shall return below.

† Pure uranium may be easily filed: it does not scratch

glass. It may be slightly carbed if heated in a crucible lined with carbon, and may be tempered.

Uranium is not magnetic when quite free from iron.

In the electric furnace uranium is much more volatile than iron.

Chemical Properties.—Uranium in fine powder, as prepared by electrolysis, takes fire in fluorine, burns brilliantly, and forms a volatile fluoride of a green colour. Chlorine attacks it at the temperature of 180°, and bromine at 210°, both with incandescence. The same reaction is produced in the vapour of iodine about 260° with formation of uranium iodide. All these reactions are complete. The metal obtained by Zimmermann was not attacked by the vapour of iodine, and in a current of chlorine it underwent a limited reaction, leaving in the boat an abundant residue.

Hydrochloric acid gas attacks it with incandescence at a dull red heat, yielding a stable chloride which produces a green solution in water. Hydriodic acid attacks it near a red heat.

Uranium in fine powder burns in pure oxygen at 170° and upwards, producing a very dark green oxide. Sulphur reacts about 500°, furnishing a black sulphide which is slowly attacked by hydrochloric acid, yielding hydrogen sulphide. With selenium it combines with incandescence.

As we have remarked above, uranium combines with nitrogen with the greatest ease. Fragments of the metal heated to 1000° in a current of nitrogen became covered with a yellow layer of nitride. Uranium in powder reacts with gaseous ammonia above dull redness, but without incandescence, producing an escape of hydrogen and leaving a black crystalline powder, which we are now examining.

Pure uranium in very fine powder decomposes water slowly at ordinary temperatures and more rapidly at 100°. This property approaches it to iron, since, according to our colleagues Troost and Hautefeuille, reduced iron decomposes water at its boiling point.

Melted uranium in contact with water is covered with a layer of oxide; this action is strikingly accelerated by the presence of carbonic acid.

Analysis.—In all these researches the uranium has been separated and determined in the form of U_3O_8 , and the carbon weighed as carbon dioxide.

Double uranium-sodium chloride yielded on analysis the following figures:—

	1.	2.	3.	Theory.
Uranium ..	47.9	47.7	48.2	48.08
Sodium ..	—	—	10.10	9.21
Chlorine ..	42.3	42.4	42.01	42.68

Metallic uranium prepared by sodium gave:—

Uranium	99.40	99.28
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The specimen always contained traces of the alkaline metal. The metal prepared in the electric furnace contained:—

	1.	2.	3.	4.
Uranium ..	99.121	99.106	98.021	99.520
Carbon ..	0.168	0.601	1.356	0.005
Slag ..	0.187	0.204	0.303	0.421

Uranium obtained by electrolysis:—

	1.	2.
Uranium	99.27	94.48
Insoluble in nitric acid ..	0.52	0.27

Conclusions.—Metallic uranium may be easily obtained either by decomposing the double uranium and sodium fluoride with sodium, or by the electrolysis of the same compound, or preferably by reducing uranium oxide with carbon in the electric furnace. These three methods yield good results, and for these researches we have had occasion to prepare more than 15 kilos. of metallic uranium.

Uranium may be obtained crystallised; the pure metal has properties approaching those of iron. It can be filed,

carbided, tempered, and oxidised in the same manner. Its tendency to combine with oxygen is greater than that of iron; in fine powder it decomposes water slowly in the cold; its reaction with the hydracids is also more energetic than that of iron. It has a most powerful affinity for nitrogen, and without special precautions the product obtained always contains a certain quantity of this element.

This metal when quite free from iron has no action upon the magnetic needle, and in the electric furnace it is much more volatile than iron.—*Comptes Rendus*, cxxii., p. 1088.

ACIDIMETRIC ESTIMATION OF VEGETABLE ALKALOIDS. A STUDY OF INDICATORS.*

By LYMAN F. KEBLER.

(Concluded from p. 288).

THE next step was to investigate the adaptability of the above process to crude morphine and crude cocaine. The results are as follows:—

Indicators.	Crude morphine.		Crude cocaine.	
	LaWall.	Kebler.	Kebler.	
Brazil wood ..	99'23	98'47	95'90	
Cochineal ..	100'14	99'53	97'11	
Hæmatoxylin ..	99'08	97'59	95'74	
Litmus ..	99'50	98'93	96'82	
Methyl orange	102'10	100'02	100'14	

With the same crude morphine the ash method yielded 97'59 per cent, the lime-water method 98'22 per cent, and the absolute alcohol method 98'33 per cent of pure morphine.

A complete analysis was made of the crude cocaine to ascertain how nearly the titrations corresponded with the gravimetric process of Dr. Squibb (*Ephemeris*, iii., 1171).

	Per cent.
Moisture	0'405
Cocaine nearly pure.. .. .	97'300
Material soluble in ether	0'100
Material insoluble in ether	1'810
Loss	0'385
Total	100'000

Notwithstanding the fact that crude alkaloids claim considerable attention on the part of the analyst, yet only a few are found already extracted on the market. It generally happens that the operator is requested not only

to determine the amount of pure alkaloids, but also to extract them from their natural sources. For this purpose the writer employed a modification of Keller's process. The method is as follows:—Place 10 grms. of the dry drug into a 250 c.c. flask; add 25 grms. of chloroform, 75 grms. of ether, stopper the flask securely, agitate well for several minutes, add 10 grms. of 10 per cent ammonia water, then agitate frequently and during one hour. On adding 5 grms. more of 10 per cent ammonia water and shaking well, the suspended powder agglutinates into a lump, the liquid becomes clear after standing a few minutes, and can be poured off almost completely.

1. When the mixture has completely separated, pour off 50 grms. into a beaker, evaporate the solvent on a water-bath, add 10 c.c. of ether, and evaporate again. Dissolve the varnish-like residue in 15 c.c. of alcohol, with heat, add water to slight permanent turbidity, the requisite quantity of indicator, and an excess of the acid solution; re-titrate with the centinormal alkaline solution.

2. When the mixture has completely separated pour 50 grms. into a separatory funnel, treat at once with 20 c.c. of acidulated water. After thorough agitation and complete separation, remove the aqueous solution into a second separatory funnel. Repeat the above operation twice more successively with 15 c.c. of slightly acidulated water. The acidulated water in the second separatory funnel is rendered alkaline with ammonia water, the alkaloid removed successively with 20 c.c., 15 c.c., and 15 c.c. of a mixture of three parts (by volume) of chloroform and one part of ether. Collect the chloroform-ether mixture in a tared beaker, and distil off the solvent. The varnish-like residue is twice treated with 8 c.c. of ether, evaporated on a water-bath, and dried to constant weight on the water-bath. The varnish-like residue is next dissolved in 15 c.c. of alcohol, and treated as in 1 above.

Nux vomica and ipecac root were treated according to processes 1 and 2; belladonna leaves according to process 2. The results are given below.

According to the well-established method of Messrs. Dunstan (1883, *Pharm. J. Trans.* [3], xiii., 665) and Short, the nux vomica examined contained 2'89 per cent of crude alkaloid. On carefully titrating this crude product with a volumetric acid solution, 2'12 per cent of pure alkaloid was indicated. Cochineal was used as an indicator. These figures show that this method produces an alkaloid residue containing a smaller percentage of pure alkaloid than that obtained by Keller's process.

From the results embodied in this paper it can safely be concluded that methyl orange cannot be numbered with the indicators suitable for titrating alkaloids. With centinormal, fifth decinormal, and other solutions of various strengths, it fails to give satisfactory results.

* Read at the Springfield Meeting. From the *Journal of the American Chemical Society*, vol. xvii., No. 10, October, 1895.

	Per cent of alkaloids in nux vomica by process 1.		Per cent of alkaloids in nux vomica by process 2. Gravimetrically.		Per cent of alkaloids in nux vomica by process 2. Volumetrically.		Per cent of alkaloid in ipecac root by process 1.	
	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.
Brazil wood..	2'04	2'58	2'94	3'00	2'37	2'37	2'46	2'54
Cochineal ..	2'64	2'69	2'86	3'10	2'42	2'39	2'59	2'49
Hæmatoxylin ..	2'18	2'24	2'88	3'11	2'23	2'27	2'48	2'54
Litmus ..	2'38	2'34	2'93	3'05	2'55	2'37	2'55	2'57
Methyl orange ..	3'02	3'64	2'93	3'02	2'65	2'61	2'95	3'30
	Per cent of alkaloid in ipecac root by process 2. Gravimetrically.		Per cent of alkaloid in ipecac root by process 2. Volumetrically.		Per cent of alkaloids in belladonna leaves by process 2. Gravimetrically.		Per cent of alkaloids in belladonna leaves by process 2. Volumetrically.	
	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.
Brazil wood..	2'58	2'60	2'36	2'35	0'26	0'20	0'19	0'15
Cochineal ..	2'63	2'68	2'52	2'33	0'28	0'20	0'24	0'14
Hæmatoxylin ..	2'58	2'68	2'35	2'33	0'27	0'22	0'21	0'13
Litmus ..	2'62	2'60	2'40	2'25	0'24	0'18	0'20	0'15
Methyl orange ..	2'66	2'63	2'89	2'61	0'25	0'20	0'23	0'20

Notwithstanding the sensitiveness claimed for it, the writer believes that its days, as an ideal indicator, are numbered. Even Professor Lunge, the staunch advocate of methyl orange, has admitted that a properly prepared solution of litmus is quite superior to this indicator, in inorganic estimations.

A solution of litmus prepared according to the directions herein employed is quite unsatisfactory for delicate titrations. The method proposed by Reinitzer promises to be better suited.

Of the indicators thus far considered, hæmatoxylin, Brazil wood, and cochineal give very promising results. Hæmatoxylin justly claims first place, and Brazil wood the second. Other indicators will be considered in due time.

As stated above, the prime object of this investigation is to ascertain what indicators are best adapted to the titration of alkaloids; but in order to determine how reliable the results were, gravimetric determinations necessarily formed a part of the work.

When it is remembered that not only do analytical methods contain inherent limitations, but also that each operator possesses a positive or a negative equation of error, the reader will undoubtedly concur with the writer that the results are very satisfactory. Attention must again be called to the fact that the work was conducted under precisely the same conditions.

As would naturally be expected, the amount of alkaloid obtained by process 2 is smaller than that secured by process 1. A small per cent of the alkaloid may be lost during the process of extraction. The small amount of colouring-matter possibly vitiates the results, or perhaps some non-alkaloidal substance increases the yield in process 1.

From the hundreds of assays made by the author, he feels justified in stating that all of the gravimetric processes yield products containing considerable non-alkaloidal matter, and hopes that the day is not far distant when all gravimetric results will at least be supplemented by volumetric methods, if not displaced by them.

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PHOTOMETRIC METHOD

FOR THE

QUANTITATIVE DETERMINATION OF LIME AND SULPHURIC ACID.

By J. I. D. HINDS.

(Concluded from p. 287).

For Calcium Carbonate.

In the investigation of lime I used a solution of calcium chloride whose strength corresponded exactly to 0.001 gm. of CaCO_3 to the c.c. Ten c.c. of this solution were taken and diluted with 20 c.c. water; then enough solid ammonium oxalate was added to precipitate the whole of the calcium. The solution was then poured into the photometric cylinder and the depth measured as in the case of the sulphuric acid. Portions of 10 or 20 c.c. of water were successively added and the depth observed after each addition. The results are given in the following table. In column 1 is the number of the solution; col. 2 shows the per cent of CaCO_3 ; cols. 3, 4, 5, 6, and 7 contain the measured depths of the liquid at which the flame became invisible; col. 8 contains the means of these depths; and col. 9 the product of these means by the per cents in col. 2, represented as before by xy . The three determinations in the fifth series were made simply as a check. Many other independent determinations were made in order to ascertain whether there was a change of opacity, and whether the precipitation would be different in the weaker solutions. No material difference was found.

	P.c. y.	C.m.	C.m.	C.m.	C.m.	C.m.	x.	xy.
1.	0.0333	2.1	2.3	2.3	2.3		2.250	0.0750
2.	0.0250	2.8	2.9	2.9	2.9		2.875	0.0718
3.	0.0200	3.5	3.6	3.5	3.5		3.525	0.0705
4.	0.0167	4.1	4.2	4.1	4.1	4.2	4.14	0.0691
5.	0.0143	4.7	4.8	4.7	4.7		4.725	0.0676
6.	0.0125	5.3	5.5	5.3	5.3		5.35	0.0669
7.	0.0111	6.0	6.1	5.9	6.0		6.0	0.0666
8.	0.0100	6.6	6.8	6.6	6.7		6.675	0.0668
9.	0.0091	7.3	7.4	7.3	7.4	7.4	7.36	0.0670
10.	0.0083	8.0	8.0	8.0	8.1		8.03	0.0666
11.	0.0077	8.8	8.6	8.6	8.8		8.7	0.0670
12.	0.0071	9.5	9.3	9.3	9.5		9.4	0.0667
13.	0.0067	10.2	9.9	9.9	10.1	9.9	10.0	0.0670

Examining the various values of xy , we find that they are not constant. They diminish rapidly at first, then more slowly. The equation is, therefore, not so simple as in the case of the sulphuric acid. It appears, however, to be a hyperbola, and we may assume that its equation has the form—

$$xy + by = a,$$

in which b and a are constants whose values are to be determined. Substituting the values of x and y from the above table we obtain thirteen observation equations. The values of a and b are then found according to the method of least squares by forming and solving the two sets of normal equations. The first set will be the same as the observation equations; the second set is obtained

by multiplying each equation by its coefficient of b . These equations are as follows:—

$$\begin{array}{ll} 0.0750 + 0.0333 b = a & 0.002500 + 0.001111 b = 0.0333 a \\ 0.0718 + 0.0250 b = a & 0.001795 + 0.000625 b = 0.0250 a \\ 0.0705 + 0.0200 b = a & 0.001410 + 0.000400 b = 0.0200 a \\ 0.0691 + 0.0167 b = a & 0.001151 + 0.000271 b = 0.0167 a \\ 0.0676 + 0.0143 b = a & 0.000967 + 0.000204 b = 0.0143 a \\ 0.0669 + 0.0125 b = a & 0.000836 + 0.000156 b = 0.0125 a \\ 0.0666 + 0.0111 b = a & 0.000740 + 0.000123 b = 0.0111 a \\ 0.0668 + 0.0100 b = a & 0.000668 + 0.000100 b = 0.0100 a \\ 0.0670 + 0.0091 b = a & 0.000610 + 0.000083 b = 0.0091 a \\ 0.0666 + 0.0083 b = b & 0.000553 + 0.000069 b = 0.0083 a \\ 0.0670 + 0.0077 b = a & 0.000516 + 0.000059 b = 0.0077 a \\ 0.0667 + 0.0071 b = a & 0.000474 + 0.000050 b = 0.0071 a \\ 0.0670 + 0.0067 b = a & 0.000449 + 0.000045 b = 0.0067 a \end{array}$$

Adding the equations together we have—

$$0.886 + 0.1818 b = 13a \quad 0.012668 + 0.003304 b = 0.1818 a$$

Dividing by the coefficient of a and eliminating, we have—

$$a = 0.0642 \quad b = -0.3$$

The required equation is therefore—

$$xy - 0.3b = 0.0642,$$

or solving for y —

$$y = \frac{0.0642}{x - 0.3}$$

This is the equation of an hyperbola referred to one of its asymptotes as the axis of x , and to an axis of y three-tenths of a centimetre to the left of the other asymptote. The curve is shown by the lax upper line in the diagram. The dotted line is the asymptote.

As an example, let us suppose that the observed depth is 4.7 c.m. Subtract 0.3 and divide 0.0642 by the remainder. The quotient, 0.0146, is the per cent of CaCO. Dividing this by 1000, we have 14.6 parts to the 100,000.

For the per cent of CaO the equation is—

$$y = \frac{0.0360}{x - 0.3}$$

To determine the probable error, we may, as before, compare a set of observations with the numbers computed from the equation as follows:—

x .	Strength used.	Strength computed.	v .	v^2 .
2.9	0.0250	0.0247	0.0003	0.00000009
3.5	0.0200	0.0201	0.0001	0.00000001
4.1	0.0167	0.0170	0.0003	0.00000009
4.7	0.0143	0.0146	0.0003	0.00000009
5.35	0.0125	0.0127	0.0002	0.00000004
6.0	0.0111	0.0112	0.0001	0.00000001
6.7	0.0100	0.0100	0.0000	0.00000000
7.4	0.0091	0.0091	0.0000	0.00000000
8.0	0.0083	0.0085	0.0002	0.00000004
8.7	0.0077	0.0077	0.0000	0.00000000
9.4	0.0071	0.0071	0.0000	0.00000000
10.0	0.0067	0.0066	0.0001	0.00000001

$$\text{Sum, } \Sigma v^2 \dots \dots 0.00000038$$

Using the same value for error as before, in which in this case n , the number of observations is 12, and q , the number of constants in the equation, is 2, we have—

$$r = 0.6745 \sqrt{\frac{0.00000038}{12-2}} = 0.00013 \text{ p.c.}$$

That, is the probable difference between an observed and computed strength of a solution is 0.00013 per cent, or 1.3 parts in a million.

Sources of Error.

The principal sources of error in the method are two. In the first place a light of constant intensity should be

used. It makes but little difference what the light is, so it is the same as that with which the constant is determined. I employed the flame of an ordinary candle as the most convenient. A brighter and steadier light would give better results. Any change of light would of course change the constants in the equations.

The second source of error is the personal equation. Each individual can determine this for himself. The error dependent upon the eye can be almost eliminated by using it in the usual way, that is with or without glasses.

Each individual can obtain the constants for himself by making a few determinations with solutions of known strength. The best strength to use is that between 0.01 and 0.02 per cent. Great care must be taken in measuring. If 10 c.m. of a decinormal solution are taken, a difference of one drop in the measurement may make an error ten times as great as that involved in the method. So also I found that a difference of 5° in temperature was sufficient to sensibly affect the determinations.

Practical Application.

I have so far used the method and tested it only in sanitary water analysis and in the analysis of urine. To the water analyst it will be of great value. It gives the lime and sulphuric acid with almost the accuracy of the gravimetric method. It is more accurate than the soap test and is but slightly affected by the presence of magnesium salts. Of course the water must be clear.

For determining the sulphuric acid in urine I found it quite satisfactory. The urine has to be diluted with nine volumes of water, and then the colour does not sensibly affect the determination.

I see no reason why this method may not be satisfactorily used for approximate determinations with all fine white precipitates. It is not applicable to precipitates which settle rapidly or gather quickly into flakes. Whether coloured precipitates may be determined in this way is still to be investigated.

I desire to acknowledge obligations to Professor A. H. Buchanan for assistance in determining the equations and probable errors.

Chemical Laboratory, Cumberland University,
Lebanon, Tenn., U.S.A.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, June 9th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to

oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined all were found to be clear, bright, and well filtered.

The prolonged drought in the Thames Valley has been even more marked during this month than in several of the preceding months of this year; the total rainfall at Oxford for May was 0.2 inch, of which 0.15 inch fell on the 21st; the 30 years' average being 1.83 inches, there is a deficiency of 1.63 inches, or 89 per cent, for the month. The total deficiency for this year is now 4.69 inches, or more than 50 per cent on the 30 years' average.

Our bacteriological examinations gave the following results:—

	Colonies per c.c.
Thames water, unfiltered	1301
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	34
Ditto ditto lowest	12
Ditto ditto .. (12 samples) mean	21
New River water, unfiltered	950
New River water, from the Company's clear water well	25
River Lea water, unfiltered	1216
River Lea water from the East London Com- pany's clear water well	73

These results show that the London water supply is thoroughly and efficiently filtered, and that the condition of the rivers leaves little to be desired.

The chemical composition of the waters shows that the organic carbon and organic nitrogen are exceptionally low.

The following table gives the difference in chemical composition of the five Thames-derived supplies for the months of May, 1895 and 1896:—

Common Salt. Per gall. Means.	Nitric Acid. Per gall. Means.	Oxygen. Hardness. Degrees. Means.	Organic reqd. Per gall. Means.	Organic Carbon. Per gall. Means.	Organic Carbon. Per gall. Max.	Colour. Br'n: Blue. Means.
May, 1895. 1'994	0'908	14'41	0'045	0'128	0'206	13'5:20
1896. 2'055	0'871	15'89	0'033	0'064	0'078	10'6:20

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 4th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 291).

Of the following papers that marked * were read:—

*73. "On Magnetic Rotatory Power, especially of Aromatic Compounds." By W. H. PERKIN, LL.D., Ph.D., F.R.S.

This paper gives an account of the apparatus used in measuring molecular rotations, at temperatures up to about 100°, also particulars concerning the determinations of boiling-points and densities, with a description of the apparatus used for the latter purpose when it is necessary to determine them up to temperatures of about 100°, and also for substances which are solid at ordinary temperatures.

The results obtained on determining the rotation of mixtures of compounds where the specific rotations are

wide apart, and of those where they are nearly identical, are then considered, and it is seen that, under the first circumstances, rotations are obtained which are not the mean of those of the constituents of the mixture, but lower, whilst in the latter case they are the mean of the two. The most striking differences obtained are those with mixtures of ethylic nitrate and carbon disulphide.

The next subject is that of the influence of varying temperatures on the rotations. The results obtained show that all substances yet examined, water excepted, fall slightly in rotation as the temperature rises. The amount varies with different classes of substances.

This difference in the change of rotation is called the *temperature-difference*, and the results are analogous to those obtained when the refractive power of compounds is determined under similar circumstances. The rotation of water, which does not fall with the density, as with other substances, evidently increases slightly with rise of temperature. This is thought to be due to the breaking down of molecular complexes.

The next section refers to the magnetic rotations of aromatic compounds, and comprises ethereal salts, mixed oxides containing phenyl and alcohol radicles, &c., phenylic salts of the fatty acids, hydrocarbons, phenols, alcohols, aldehyds, ketones, nitriles, nitro-compounds, haloid and sulphur compounds, amines, unsaturated compounds, &c.

From the results obtained with these different classes of substances it is seen that there is a great difference between the rotations of aromatic and fatty compounds, the effect of the nuclei contained in them greatly influencing the rotation.

It is found that in many cases the substances behave like double molecules, the part containing the fatty groups acting like a fatty compound, whilst that containing the nucleus acts in a different manner. This occurs more especially where a carbonyl group exists between the nucleus and the fatty groups, in which position it acts like a screen between them. Some other groups also behave in this manner more or less effectively.

The nucleus is also influenced by the groups and haloids it is associated with; thus with nitroxyl and fluorine its influence is greatly reduced, and it is also reduced, but not to nearly so large an extent, by carbonyl, and also by chlorine; all being strongly electro-negative elements and groups. On the other hand, it is much increased by association with hydrocarbon groups, especially when unsaturated, and greatly by the electro-positive amidogen group and its methylated and phenylated derivatives.

With reference to the effect produced by the nitroxyl group, it is thought that possibly the oxygen in this compound may be in a para-magnetic condition, as oxygen is when in the free state, and especially when in the liquid condition. If so, this would account for the very low rotation of this compound, as it would have a negative rotation. If this be so, the inference is that fluorine is also paramagnetic; the very low rotation of sulphuric acid and phosphoric acid, containing sulphur and phosphorus, which have very large rotations, would also become easily explainable if the oxygen they contained were paramagnetic.

The variation in the influence of the nucleus on the rotation was found to be very considerable, even in hydrocarbons, the influence increasing as two or more nuclei become more and more nearly associated, and at last come into direct union, as in diphenyl. This, however, does not appear to arise from mass action.

The effect produced by the association of the benzene nucleus with the unsaturated group $-\text{CH}=\text{CH}-$ is also found to be very remarkable, and especially so when two are united with it, one on each side, as in stilbene, the result being nearly ten times as great as when this group is in the fatty compounds.

From the results obtained it is evident that no fixed value can be found for phenyl in hydrocarbons or other

aromatic compounds, nor yet for naphthyl; at the same time the rotations do not give any constant values for the groups which are directly associated with the nucleus. Thus, the influence of NH_2 entering a paraffin raises its rotation by 0.971, but in benzene 4.792, and in naphthalene, for the α -position, 12.353. From these results it is seen that it would be absurd to assume that this group has these widely different values, or that the carbon and hydrogen in the nucleus has changed so as to share in this great increase. It is noticed also that these great changes take place in cyclic compounds only.

The fact that in naphthalene both nuclei are apparently equally affected by the introduction of nitroxyl or amidogen, although the displacement taking place is one only, suggests that there is a kind of inductive influence going on in these compounds from one carbon to the other; especially as the effect of some of the groups approximates to the ordinary influences found in the fatty series, multiplied by the number of carbon atoms in the nuclei, the amount being sometimes rather lower and sometimes rather higher. Taking aniline as an example, the increase in rotation for the amidogen group in the nucleus, although not six times as great as the ordinary influence of amidogen in the fatty series, is yet nearly five times that amount. In the naphthalene series it is rather more than ten times as great in the β -compound, whilst in the corresponding α -compound it is twelve times as great.

Diphenylamine affords an interesting example in this connection, the two separate molecules being united by NH . The influence it exerts appears to be not much less than twice that of this group in aniline, both nuclei being evidently equally influenced.

From these results it appears that these great changes in rotation must be chiefly due to physical influences, and that only a part of their effect can be attributed to the rotatory power of the atoms contained in the molecule.

The high refractive power of these compounds apparently must also be due to the physical nature of the molecules, and not simply to their chemical composition.

It is considered doubtful whether only one kind of physical condition would account for all that takes place in such compounds containing the benzene nucleus, as besides smallness and largeness of rotation, there are other differences to be accounted for.

The physical conditions due to the arrangement of the atoms in the molecules of saturated carbon compounds, being more simple than those connected with the unsaturated or cycloid compounds, have only a comparatively small influence on the rotation, yet each series of these compounds has an initial influence of its own, dependent on the series group, or special molecule, such as COOH , CO , COH , OH , &c., and for calculating the rotations of members of these different series, a set of *series constants* had to be prepared. These variations cannot evidently be due to change in the rotatory power of the elements, but must be caused by the physical conditions induced by molecular arrangement.

On considering the refractive power of saturated compounds, it is found that similar variations occur in the different series. Thus the paraffins, mono- and poly-hydroxy-compounds, or alcohols, give relatively higher results than the aldehyds, fatty oxides, and ethereal salts. Formic acid and its ethylic salt being exceptional, as in the case of the rotations.

These fluctuations in the refractions must, therefore, be real, and not due to experimental errors, and the influences modified as in the rotation, by molecular arrangement, the so-called value used in calculations being only the average influences which the elements exert in different compounds. These must not be regarded as physical constants.

It is at present impossible to determine with certainty the relationship of these influences to the true value of the elements, especially as there are few elements suitable

for examination, and even these are usually molecular groups, but the evidence, though scanty, points to the probability of the true values of the elements not being largely different from the average influence they exert in the ordinary saturated carbon compounds, though perhaps rather higher.

In saturated cyclic compounds the structure is, as might be expected, also simple, and like that of ordinary open chain compounds, because the influence of the CH_2 groups contained in both is apparently practically the same. But directly unsaturated groups occur in open chain compounds, and consequently greater molecular complexity of the molecule exists, larger rotations and higher refractive power manifest themselves, and these increase with each repetition of the unsaturated group, notwithstanding that there is a loss of H_2 in composition each time. When, however, these unsaturated groups are united, so as to form a cyclic compound, a much greater effect is produced, both on rotation and refraction, evidently due to the formation of a new molecular system.

Considering these products from the saturated to the unsaturated, and then to the cyclic condition, each step being accompanied with a reduction of H_2 , and at the same time a 'rise' in rotation and refraction, and then a still larger increase on the formation of the nucleus, it becomes evident that it is the increase of molecular complexity that is the cause of the augmentation of these properties, and that it is not the composition of the substance which produces the effect. It would be difficult to believe that the true rotation or refractive power of an element could be a variable quantity.

Whilst the influences given for the rotations and refractive power of the elements in the fatty series are not true values, yet this does not militate against their usefulness as a means of judging the constitution of compounds. The same is also true of the apparent values of phenyl and the effect of other groups in the aromatic series.

74. "Mononitroguaiacol." By RAPHAEL MELDOLA, F.R.S.

In the course of some investigations on phenol derivatives, not yet complete, the author had occasion to prepare mononitroguaiacol. As this compound does not appear to have been described before, and as the author learns that other investigators are engaged on the same subject, the following note on the method of preparation may be found of use. The difficulty in nitrating guaiacol directly is to prevent the nitration going too far, so as to avoid the formation of dinitroguaiacol on the one hand, or, on the other hand, complete destruction of material. The action of nitric acid on guaiacol is rendered quite manageable by acetylating or benzoyleating the compound as a preliminary step. The acetyl derivative is an oil (Tiemann and Koppe, *Ber.*, xiv., 2020); the benzoyl derivative is readily formed by the action of benzoyl chloride on guaiacol in the presence of sodium hydroxide in aqueous solution. Crystallised from dilute alcohol it forms small rhombohedra, melting at $58-59^\circ$. In order to nitrate the acetyl derivative, it is mixed with about an equal volume of glacial acetic acid, and a considerable excess of fuming nitric acid is gradually added to the well-cooled mixture. It is advisable to dilute the nitric acid at first with glacial acetic acid, but the undiluted acid may subsequently be added in small portions, if the contents of the flask are not allowed to become warm. The condition essential for success may be briefly described as being rapid nitration at a low temperature; if allowed to stand too long dinitroguaiacol is formed. The great excess of nitric acid is necessary to form the mononitro-derivative rapidly. The whole operation takes from one and a half to two hours, and the completion of the nitration is best ascertained by stirring a few drops of the solution vigorously with water on a watch-glass. If the oily deposit does not solidify on being stirred with water in the course of a few minutes, more nitric acid is required; when the oily drops soon become crystalline

under the conditions mentioned, the whole contents of the flask must be stirred into cold water in a thin stream, and allowed to stand for some hours. The solid mononitroguaiacol acetate is collected, washed with water, and purified by crystallisation from boiling water. The compound separates on cooling in small, whitish needles, having a melting-point of $101-102^{\circ}$.

0.0985 gave 5.6 c.c. moist nitrogen at 13.5° and 764.8 m.m. = 6.73. The formula $C_6H_3(NO_2)OCH_3 \cdot OC_2H_5O$ requires N = 6.63 per cent.

It is probable that two nitro-derivatives, an ortho- and a para-, are formed during this process, but the orthonitro-compound is present only in small quantity, and is removed by the process of crystallisation. The final product is most probably the paranitro-compound, $C_6H_3(NO_2)OCH_3 \cdot OH$ (4:2:1), for reasons that will appear subsequently. The acetyl derivative is readily hydrolysed by boiling with dilute caustic alkali for a few minutes. An orange solution of the alkaline salt of nitroguaiacol is obtained, and, on acidifying, the nitroguaiacol separates out in the form of whitish ochreous needles. After purification by crystallisation from hot water, it has a melting point of 104° .

0.0732 gave 5 c.c. moist nitrogen at 12° and 771.2 m.m. = 8.22. The formula $C_6H_3(NO_2)OCH_3 \cdot OH$ requires N = 8.27 per cent.

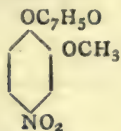
Benzoylguaiacol is nitrated in acetic acid by the same method as that described for the acetyl derivative, and, on the whole is a more satisfactory compound to work with. The first action of the nitric acid is the formation of an oily product, which does not solidify in water, possibly a nitrate. When sufficient nitric acid has been added, the oily deposit solidifies in water, as before, but vigorous stirring on the watch-glass is necessary to promote crystallisation. The benzonitroguaiacol thus obtained consists of a mixture of two modifications, which can be separated by crystallisation from alcohol. The chief product, which separates out first, consists of prismatic needles, melting at $102-103^{\circ}$. The mother-liquor deposits the other modification on standing, in the form of rhombic plates, which, after two or three crystallisations from alcohol, have a melting-point of $88-89^{\circ}$.

0.0976 (needles) gave 4.15 c.c. moist nitrogen at 14.5° and 765.9 m.m. = 5.01.

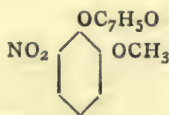
0.1078 (plates) gave 4.8 c.c. moist nitrogen at 19° and 764.1 m.m. = 5.12.

The formula $C_6H_3(NO_2)OCH_3 \cdot OC_2H_5O$ requires N = 5.12 per cent.

Although no direct proof of the constitution of these two nitro-derivatives has been obtained as yet, there is every reason for believing that they are the ortho- and para-compounds.



M. p. $109-103^{\circ}$.



M. p. $88-89^{\circ}$.

This view, so far as relates to the para-compound, is borne out by the fact that the nitro-guaiacol of m. p. 104° obtained by the hydrolysis of the acetyl derivative of m. p. $101-102^{\circ}$, gives the same benzoyl derivative (m. p. $102-103^{\circ}$) on treatment with benzoyl chloride and alkali in the usual way. It may be pointed out that the paranitro-derivative has been prepared more especially with a view to the direct synthesis of eugenol and related compounds, since the replacement of the nitro-group by halogens, and subsequently by allyl, should give rise to the formation of benzoeugenol.

In carrying out these experiments much valuable assistance has been rendered by Mr. Edward J. Wray.

NOTICES OF BOOKS.

Kelly's Directory of Chemists and Druggists. This work includes Manufacturing Chemists, Wholesale Druggists, Drysalters, Patent Medicine Vendors, and other Trades connected therewith, of England, Scotland, and Wales, and most of the Principal Towns in Ireland. Eighth Edition. London: Kelly and Co., Ltd. 1896. 8vo. Pp. 807.

We must pronounce this Directory very useful, both from our own examination and from information which reaches us through private channels. At the same time, whilst fully aware that Messrs. Kelly must know their own business best, we cannot help thinking the arrangement of trades and professions here adopted very singular. Supposing that analytical and consulting chemists, assayers, and chemical manufacturers should be associated with the chemists and druggists, we do not see why hospitals, photographers, dealers in "patent" medicines, dentists, and veterinary surgeons should be here included. These two bodies might, we submit, be more suitably introduced into a medical directory, whilst certain other trades which figure here would be more at home in a "Quack Directory," if such a work could be safely or justifiably published. The photographers might perhaps better figure in an Art Directory. Perhaps such arrangements might occasion an excess of matter in some of Messrs. Kelly's Directories, and a deficiency in others.

Chemistry in Daily Life: Popular Lectures. By Dr. LASSAR-COHN. Translated by M. M. PATTISON MUIR, M.A., Fellow of Gonville and Caius College, Cambridge. With 21 Woodcuts in the Text. London: H. Grevel and Co. 1896. Pp. 324.

THIS book reminds us, by its title, very closely of a work of British origin which has met with general approval and has gone through several editions. Prof. Pattison Muir observes, in his Preface, that "chemistry is emphatically the most human, and for that reason the most fascinating, of the Sciences,"—an assertion which will not be universally admitted. "Vague notions," the translator tells us, "circulate in men's minds concerning chemistry. Some think the chemist is a man who compounds drugs and mixes pills,"—an error, we must add, exclusively British. The dispenser of medicines is called in France "pharmacien," and in Germany "apotheker."

The author sets out with respiration, the maintenance of animal heat and combustion, passing on to flame, candles, the elements, chemical formulæ, atoms and molecules, coal-gas and the nature of flame.

The third chapter introduces us to the chemistry of agriculture, to the diet of men and other animals, fibrin, serum, artificial fodder, and gelatin.

In the fourth lecture we are taught the importance of a mixed diet, to the question of bounties on exported sugar—a procedure by which several Continental countries waged, and still wage, a war against Britain.

In the fifth lecture we find an account of the dietetic values of the chief foods, of fermentation, and the various alcohols.

In dealing with these subjects Prof. Lassar-Cohn has not been able entirely to avoid stroking the vegetarians and the "temperance" party against the grain. (See p. 119).

In the sixth lecture we pass to vinegar, wood-spirit, and the Greek fire, gun-cotton, which the author admits has come out victorious in all contests with melinite, which is not much spoken of. Dynamite is said to have come into favour for the peaceful purpose of mining, and also, it might have been added, for the operations of socialists, anarchists, and nihilists. Blasting gelatin, the mixture of gun-cotton in nitro-glycerin, is rightly pronounced the most energetic explosive at our disposal.

From explosives Prof. Lassar-Cohn takes a leap to clothing materials, speaking of shoddy and mungo as artificial wool—a rather misleading expression. Tanning comes next in its various modifications, such as chrome- and iron-tanning. The leathers obtained by these two procedures have not given satisfaction in Europe, though a chrome-leather is still produced in America.

Bleaching and dyeing next engage the reader. Prof. Lassar-Cohn seems to hope that artificial indigo may yet be produced cheaply enough to compete with or supersede the natural colour, an aspiration in which we by no means share.

In the latter part of the book we find, among other things, a dissertation upon bimetalism, strangely out of place. The Röntgen rays are also described, so are also the modern disinfectants and the ammonia process for the manufacture of soda, though without any mention of its first discoverers.

The defect of this work, as far as English readers are concerned, is its predominating German point of view, e.g., the remarks on beet-sugar, on rye-bread, &c. In other respects the book will prove valuable and instructive.

Water Supply (considered principally from a Sanitary Standpoint). By WILLIAM P. MASON, Professor of Chemistry, Rensselaer Polytechnic Institute; Member of American Philosophical Society, American Chemical Society, American Water-Works Association, New England Water-Works Association, Franklin Institute, &c. First Edition; first thousand. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1896. 8vo.

We have here a work of very considerable value. With the increase of population, especially in the river valleys and the collecting area whence the streams must receive their supplies, the difficulty of obtaining an adequate quantity of a trustworthy water has increased, and must still further increase.

Our author, in his introductory chapter, fully appreciates the abundance and the excellence of the water supplied to ancient Rome.

The second chapter treats of drinking-water and disease. The connection between bad water and certain of the most alarming types of disease is no longer open to discussion, but the question still exists—What waters are to be regarded as bad? Swamp waters, such as those of the Dismal Swamp of Virginia, and the *aguas negras* of certain affluents of the Orinoco, though loaded with dissolved organic matter, are not found to occasion troubles, whilst the beautifully clear waters from certain wells in London (now disused), and the drainage from the rice-fields of India, are almost more than dangerous. According to Schröder, here quoted, peat-dust kills the spirillum of cholera in five hours. Laveran concludes, from his experience, that travellers in malarial districts find that they may very generally escape intermittents by boiling the drinking-water. The authorities here quoted are far from considering polluted water the only channel for the malarial poison. African friends tell us that in certain districts the water-melons are full of malaria, and caution new-comers against their use. The presence of decomposing sawdust in streams is pronounced by Dr. Mulhern, of the Michigan Board of Health, a source of malaria. Parke's "Hygiene" is quoted to show that dangerous waters may be made safe by a previous treatment with alum. The ground seeds of *Stychnos potatorum* are successfully used for the same purpose in tropical Asia and Africa. The celebrated Lausen case is here cited, and is valuable as showing that the passage of foul waters over or through soil is no sure method for their purification.

The account given (pp. 48 to 51) of the disease spread by the great pilgrimages in India is horrifying. But the

case concerning the sanitary state of China is much worse than our author makes it appear.

In a note the author recognises the fact that common flies may aid in distributing cholera. This holds good with the zymotic diseases.

Mr. Mason's work is a storehouse of facts interesting to the sanitarian, and deserves a very wide circulation. The only error which we find in it is the statement that the notorious "Recommendations" of the late Rivers' Pollution Commission in this country now form part and parcel of British sanitary law.

CORRESPONDENCE.

ON THE SPECTRAL AND OTHER PROPERTIES OF THALLIUM IN RELATION TO THE GENESIS OF THE ELEMENTS.

To the Editor of the Chemical News.

SIR,—The posthumous publication, in successive numbers of the CHEMICAL NEWS from October last to the present month, of the Spectroscopic Studies of Jean Servais Stas, is opportune in view of the strong conviction which now prevails in the minds of many eminent chemists and physicists, that the elements have been evolved from a primordial substance of small specific gravity and of low atomic weight.

The avowed object of the distinguished Belgian chemist in undertaking these studies, as stated in his "Introduction," was to ascertain whether he could cause, by increasing the temperature or the intensity of the electric current, a correlation among the characteristic bands of the luminous spectra of compounds of the alkaline and alkaline-earth metals and of thallium, when these elements were in a state of purity.

That Stas entered upon these investigations with some degree of prejudice, and with full assurance that his non-success should be the measure of the power of all future investigators, will be evident from his own statement that "I was well aware that if my experiments failed, after having taken great pains and having devoted to this work an amount of time which I might, perhaps, have used more profitably, I should add nothing to the sum of our spectroscopic knowledge. Still, I should free Science from an hypothesis which has led astray, and may again lead astray, many clever men; it seemed to me that this was just as much helping to advance *real* knowledge."

Experimental researches undertaken in this spirit, as might have been expected, were purely negative in their results; and as some of them are in direct contradiction to those of other investigators, the interests of Science demand that these discrepancies should not be allowed to pass unnoticed.

Since the publication of my paper "On the Origin of Elementary Substances" (CHEMICAL NEWS, vol. xxxviii, p. 66), I have made many experiments on the spectra of the elements, through great ranges of temperature and pressure, with the object of effecting their mutual transformations, but hitherto without any positive result. Nevertheless, my failure to effect such spectral transformations has not diminished my belief in the ultimate solution of the problem; still less so in the theory that elementary species have been formed by the successive condensations of a primordial substance of great tenuity. No naturalist of reputation is now to be found who rejects the doctrine of the evolution of organic species from a few simple forms, on the ground that the transformation of one natural species of plant or animal into another has not so far come under man's observation. Moreover, just as the evolutionary theory of organic species derives its chief support from the artificial variations induced in plants and animals under domes-

tication, so the theory of the evolution of elementary species from a few typical elements is equally well supported through the power of modern chemists to form homologous series of the positive and negative organic radicals, which possess properties similar to those of the elements.

The spectroscopic research on thallium undertaken by Stas to disprove the doctrine of the transformation of elementary substances is interesting as showing how a distinguished chemist, with all the wealth of chemical and physical appliances at his disposal, should himself have missed the road which he expressed so much anxiety for other investigators to follow.

Long before the researches of Stas, the spark spectrum of thallium had been examined by Huggins and by Thalén. The arc spectrum of this metal has also been mapped by Liveing and Dewar, and by other investigators, far into the ultra-violet. My own researches on the spectrum of thallium, at different temperatures and from a millimetre to 80 atmospheres of pressure, led to the discovery in the arc and spark spectrum of the red line, 6560 (*Proc. Roy. Soc.*, April 20, 1893).

The discovery of this line directly correlated the spectrum of thallium with the homologous spectra of indium and gallium, and furnished the most instructive example of the mutual dependence of the properties of elements of the same series (indicating a community of origin) that is to be found in the whole range of the physico-chemical sciences.

It is now common knowledge that, within the limits of the infra-red and ultra-violet, thallium has three distinct spectra of temperature:—

1. The flame spectrum, consisting of a single green line, 5349.
2. The arc spectrum of two lines, 6560 and 5349.
3. The spark spectrum, with lines 6560, 5949, 5349, 5153, 5078, 5053, 4981, and other lines less characteristic.

Now the final result of the elaborate study of the spectrum of thallium by Stas, as stated by himself, is "that the electric spectrum of thallium consists of a single green line not capable of being split up, exactly like the flame spectrum of this metal, and that electricity is no more capable of dissociating it than heat." (The italics are as printed in the *CHEMICAL NEWS*). We have in this conclusion a direct contradiction of the results of other competent observers who have examined the spectrum of thallium. Stas would appear to have felt this difficulty, by suggesting that the spark spectrum in air may not be that of the pure metal, but of its oxide.

To set at rest the doubt thus raised, I have recently examined the spark spectrum of metallic thallium in nitrogen, produced by passing atmospheric air over red-hot copper and dried over sulphuric acid, when I found the spectrum to be the same as that obtained in air. I would here remark that the red line, 6560, of the arc spectrum is somewhat elusive, unless there is a sufficient quantity of the metal in the crater of the arc to reverse the green line, when the red line invariably shines out with marked brilliancy in all the specimens of the metal, its sulphate, carbonate, nitrate, and chloride, which I have experimented with. It is also advantageous to fill the crater with the metal, or its compounds, before the arc is struck, in order to ensure an abundance of thallic vapour during the observation.

Another method adopted by the Belgian chemist to discredit the results obtained by other investigators of the spectrum of thallium, is to be seen in his statement that "since observers have found a complex electric spectrum of thallium when using thallium they have not prepared themselves, I think I am correct in concluding that the metal they used was other than that used by Bunsen, Lecoq de Boisbaudran, and myself."

Now as there are many workers in science who, from education and habit, may still look to Stas as an authority on questions relating to spectral analysis, the multiple

relations of the atomic weights, and the genesis of the elements, I will now offer the sum of £50 to any chemist who will submit a specimen of pure thallium (not less than a cubic centimetre) which will only show the green line 5349 in the electric spectrum; and I will also contribute, on the same condition, a further sum of £100 to the Research Fund of the Chemical Society; the specimens of thallium to be tested either at the laboratories of the Owens College, or at the house of the Literary and Philosophical Society, Manchester.—I am, &c.,

HENRY WILDE.

Alderley Edge, June 19, 1896.

DOES HYDROGEN FIND ITS PROPER PLACE AT THE HEAD OF GROUP I. OR AT THE HEAD OF GROUP VII?

To the Editor of the *Chemical News*.

SIR,—In reference to the interesting paper by Professor Orme Masson contained in the last number of your valuable journal, may I be permitted to make a short quotation from a note of mine published in the *CHEMICAL NEWS* of July 12th, 1872 (vol. xxvi., p. 19):—

"Hydrogen and chlorine are here classed together on account of their mutual replaceability, with but a slight change of properties, in many chemical compounds, such as trichloroacetic acid, &c. The position, too, of hydrogen in the list of elements when arranged in the order of atomic weights, indicates that it is really the lowest member of the chlorine group."—I am, &c.,

JOHN A. R. NEWLANDS.

Laboratory, 27, Mincing Lane, E.C.,
June 23rd, 1896.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 22, June 1, 1896.

The President announced the death of M. Daubrée, the doyen of the Section of Mineralogy. It will not be forgotten that one of his constant observations was the description and classification of meteorites of every kind.

Action of Acetylene upon Iron, Nickel, and Cobalt reduced by Hydrogen.—Henri Moissan and Ch. Moureu.—Will be inserted in full.

The Respiratory Exchanges in the case of Muscular contractions occasioned Electrically in Animals Fasting or Fed upon Rations rich in Carbohydrates. Corollaries referring to the Determination of the Potential directly devoted to the Physiological Work of the Muscles.—A. Chaveau and F. Laulauré.—The potential devoted to the execution of muscular work is always a carbohydrate, either borrowed from the reserves of glycogen of the organism, or coming from the transformation of the fatty reserves or furnished more or less directly to the muscles of the digestive absorption.

On Molybdenite and its Preparation with Molybdenum.—M. Guichard.—Will be inserted in full.

On the Methylamines.—M. Delépine.—Nessler's reagent gives with dimethylamine and trimethylamine a white precipitate which disappears on the addition of water. On the contrary, it gives with monomethylamine a light yellow precipitate, which is formed with great sensitivity and which re-dissolves neither in an excess of water nor in an excess of the reagent. Sulphuric acid

dissolves it in heat, and on dilution it reappears if the heat has not been too prolonged. It blackens easily on exposure to light.

On the Phenylhydrazine Aldehydates.—H. Causse.—An account of the aldehydates of diphenylhydrazine and the benzylate of the same base.

Ceramic Stones obtained by the Devitrification of Glass.—M. Garhey.—The author uses especially bottle-glass and window-glass containing an excess of earthy bases. These materials are pulverised and devitrified by successive treatment in two furnaces. In the first furnace, which has a lower temperature, they remain for an hour, and in the second, which is much hotter, they are left for a few minutes only.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. 1, No. 3.

Report presented by H. Le Chatelier on the recent Work of Richards on Aluminium. Submitted on behalf of the Committee of the Chemical Arts.—As a solder for aluminium, Prof. Richards particularly recommends a mixture of—

Aluminium	2 parts.
Zinc	26 "
Tin	70 "
Tin phosphide	2 "

100

It should be applied without flux upon the article, previously roughened and heated, if possible above the melting-point of the solder. The alloys of aluminium with gold have a fine red colour, and are utilised in jewellery; their melting-point has been studied by Prof. Austen. Among the alloys of nickel, mention is due to "roseine" consisting of—Nickel, 40; aluminium, 30; tin, 20; silver, 10. The alloy "manganine" consists of—Copper, 67.5; aluminium, 1.2; manganese, 18; zinc, 13; tin, 5; it is remarkable for its high electric resistance, which is superior to that of German silver. Its tenacity is 25 kilos, for 1 square millimetre. The ternary alloys, containing both nickel and copper, are remarkable for their mechanical properties.

Cu	88	90	64
Ni	1	3	33
Al	1	3	3
Sn	1	6	0

The two former have a tenacity of 60 kilos. per square millimetre. The third has a superior tenacity. It is suitable for the manufacture of table cutlery.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Fluor Spar.—A correspondent wishes to know the approximate annual consumption of this mineral, the present price, and whether the English or foreign product is mostly used, and which is the better quality.

German Dictionary.—Can any correspondent recommend a German Dictionary suitable for use with German scientific literature.—IGNORAMUS.

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Gmelin's Handbook of Chemistry (Organic and Inorganic), by H. V. WATTS, complete set, 19 vols. cl., scarce, £20, for £8 8s.
Trans. Roy. Soc. of Edin., 1783 to 1890, 36 vols., 4to., h. calf, £45.
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INDEX.

- ACENAPHTHALENE** and fluorene, 254
Acetic acid distillation, 58
Acetylene and air, explosive mixture of, 222
 combustion of, 47
 photometric standard with, 59
 theory of luminosity, 68
Acid, acetic, distillation, 58
 boric, detection of, 230
 distribution in nature, 12
 bromocamphorsulphonic, oxidation products of, 208
 camphoric, derivatives, 267
 desyleneacetic, 254
 glyceric, preparation of, 293
 dibenzoylglyceric, &c., some of the ethereal salts of active and inactive, 81
 hydriodic, action of gaseous, 293
 hydrobromic, action of, 221
 hydrochloric, manufacture of, 258
 conversion of chlorine into, 197
 naphthylaminesulphonic, 54
 nitric, detection, 251
 quantities in the Seine, 186
 organic, constitution of a new, 194
 perchloric, preparation, 8, 17
 phenoxyethylmalonic, derivatives of, 104
 phosphoric, determination of, 53
 new, 48
 preparation of pure anhydrous hydrocyanic, 71
 selenic, reduction of, 285
 sulphuric, and lime, quantitative determination, 285, 299
 and potassium permanganate, distillation of aqueous solutions, 122
 synthesis of geranic, 119
 tartaric, transformation of, 257
 titanic, and iron in ores, determination of, 123
 uric, fermentation, 257
 volumetric determination of phosphoric, 212
"Acid, Sulphuric, and Alkali, Manufacture of" (review), 268
Acidic thiocarbides, &c., 230
Acidimetric estimation of vegetable alkaloids, 287, 298
Acidity of pyroligneous products, 164
Acids, cis- and trans-methylisopropylsuccinic, 152
dimethylglutaric, 152
dimethylsuccinic, 152
 first, of the fatty series, distillation of, 245
 in plants, identification of principal, 295
Acids, fluorides of, 107
 lactic and malic, ethereal salts of optically active, 229
 of the fatty series, melting and solidification points of, 65
 xylic and xylidinic, 208
Accumulator, principle of a luminous, 185
Ackroyd, W., colour of the ions as a function of atomic weight, 221
 and M. Knowles, permeability to Röntgen rays, 140
"The Old Light and the New" (review), 293
Acoustic analysis of mixtures of two gases of different densities, 47
Adulteration laws, British, 114
Äërolite, the Madrid, 131
"Agricultural Chemistry and Zoology, Elementary" (review), 93
Agriculture, humus theory in, 96
Air, explosive mixtures of acetylene and, 222
 in the soil, circulation of, 72
 liquefaction of, and research at low temperatures, 40
Alcohol, action on mercurous iodide, 12
 molybdic acid as a reagent for, 149
Alcohols, terpenic, extraction of, 232
 toxic action of different, 293
Alcoholic liquids, solubility and activity of soluble ferments in, 12
"Alembic Club Reprints" (review), 245
"Alkali and Sulphuric Acid, Manufacture of" (review), 268
Alkaline reduction of metanitriline, 9
Allen, A. H., determination of urea, 103
Allibon, G. H., estimation of insoluble phosphate, 47, 94
Alloys of copper and zinc, 168
Alkylammonium cyanates, transformation of, 82
Alternate current arc, effect of wave-form on, 209
Alternating currents, measurement of, 290
Alumina, action in the composition of glass, 175
Aluminium from aqueous solutions, deposition of, 122
 prepared by electrolysis, sodium in, 64
 and its alloys, analysis of, 49
 report on recent work of Richards, 306
"Aluminium" (review), 141
Amalgams of molybdenum, 186
Amides, synthesis of hydrochlorates of, 48
Amido-chromates, so-called, 48
 compounds, action of diphenyl di-isocyanate on, 37
Ammoniacal silver nitrate, action of sugar on, 81
Ammonium amalgam, formation of so-called, 54
 chloride, volumetric composition of, 206
Analysis, acoustic, of mixtures of two gases of different densities, 47
 and metallurgy of copper, 117
 of alloys of lead, tin, antimony, and arsenic, 25
 aluminium and its alloys, 49
 of chrome-iron ore, ferro-chromium, and chrome-steel, 1
 of tin slag, 58
 of water from the dropping well at Knaresborough, 196
 volumetric, of a mixture of chlorides, hypochlorites, and chlorates, 157, 169
"Analysis of Single Salt" (review), 163
"Analysis of Spectrum" (review), 273
"Analysis of Water" (review), 196
"Analysis, Qualitative, Laboratory Tables for" (review), 163
Analytical gas apparatus, 158
 study of the alternating current arc, 116
Anderlini, F., and R. Nasini, detection of argon, 233
Andrews, L., analysis of alloys of lead, tin, antimony, and arsenic, 25
 E. R., and R. Meldola, alkaline reduction of metanitriline, 9
Anethol, 59
Anhydride, phosphoric, molecular weight of, 103
Anhydrous hydrocyanic acid, preparation of pure, 71
Aniline, determination of, 236
 moisture in, 270
Animals, transformation of fat into carbohydrates in certain, 280
Anniversary meeting, Chemical Society, 220
Anode, X rays emanate from, 119
Anthracite assaying, 178
Appleyard, R., adjustment of the Kelvin bridge, 208
 dielectrics, 255
 J. R., and J. Walker, transformation of alkylammonium cyanates, 82
Apport, L., action of alumina in the composition of glass, 175
Aqua regia, toxicological detection of, 27
Arc, analytical study of the alternating current, 116
 effect of wave-form on the alternate current, 209
Archdeacon, W. H., and J. B. Cohen, action of sodium alcoholate, 81
Arctowsky, H., crystallisation of bromine, 197
Argon, a view on, 85
 detection of, 233
 facts about, 233
 in the natatory bladder of fishes, 164
 is it as idle as its name suggests? 47
 and helium, 259
 further details, 96
 in the gas from the Bath springs, 247
 in the system of the elements, 235
 some physical properties of, 75
 or nitrogen, separating atmospheric, 24
"Argon and Newton" (review), 143, 278
Argynopoulos, T., X rays, 230
Armstrong, H. E., inversion of asymmetric compounds, 123
 note on etherification, 127
 origin of colour, 126
 relation of pinene to citrene, 127
 and W. P. Wynne, naphthylaminesulphonic acid, 54
 tri-derivatives of naphthalene, 55
Arnaud, A., transformation of tauric acid, 257
Aromatic compounds, magnetic rotatory power of, 301
 series, isomerism in the, 186
Arsenic, compounds of selenium with, 198
 determination of, 121, 134
 in coal, 191
 and copper, separation of mercury from, 28, 38
Arth, G., calculation of the thermic power of coal, 91
Arts, Trades, and Industries Exhibition, 149
Aschoff, K., and P. Jannasch, determination of the halogens, 281
Aslanoglou, P. L., acetic acid distillation, 58
 combination of atmospheric and chemical nitrogen with metals, 115
 is argon as idle as its name suggests? 47

- Assay balance, auxiliary, 207
 Asymmetric compounds, inversion of, 128
 Atmospheric argon and nitrogen, separation of, 24
 and chemical nitrogen with metals, combination of, 115
 nitrogen, combination with magnesium, aluminium, iron, copper, &c., 35
 Atomic weight of zinc, re-determination of, 197
 revision, 226, 238, 250, 264
 weights, colour of the ion as a function of, 28
 the elements, numerical relations in, 263
 re-calculation of, 293
 "Atomic Weights, True, of the Chemical Elements" (review), 231
 Atoms, ions, and molecules, relations of the colours of, 48, 260, 271
 size of, 63
 Autenreith, W., luteol, 62
 Aymonnet, M., spectral displacement of the solar thermic maximum, 47
- BABLICH, H., and A. G. Perkin, morin, 253**
 Bacteria, living, influence of induction currents on, 233
 Bacterial toxins, action of currents of high frequency on, 119
 Bailey, H., analysis of tin slag, 88
 Baizard, L., compounds of nitroso-ruthenium, 186
 Balland, M., maize, 257
 rice preserved over a century, 221
 Barbier, P., and L. Bouveault, extraction of rhodinol, 153
 rhodinol, 166
 synthesis of geranic acid, 119
 Barium sulphate, peculiar relations of solubility of, 276
 tetrachromite, crystalline, 281
 Barnett, R. E., and W. A. Tilden, molecular weight of phosphoric anhydride, 103
 Barthelémy, Oudin, and Lanne-longue, MM., utility of photographs in human pathology taken by means of the X rays, 61
 Bassett, H., anthracite assaying, 178
 Batavian Society of Experimental Philosophy, programme, 4
 Batelli, A., and A. Garbassa, some facts relating to the Röntgen rays, 164
 Bauge, G., crystalline ammoniacal chromous carbonate, 142
 Bayrac, M., and C. Canichel, absorption of light, 95
 Beadle, C., the X rays, 94
 and O. W. Dahl, increase in the temperature of cellulose, 180
 Becquerel, H., invisible radiations emitted by the salts of uranium, 167, 189
 luminous accumulator, 185
 radiations emitted by phosphorescence, 141
 new radiations by metallic uranium, 295
 Beebe, A. C., volumetric method for lead analysis, 18
 Péhal, campholenic derivatives, 95
 Behrend, R., electrometric determination of the final point in volumetry, 270
 Benoit, L., and D. Hurmuzescu, action of X rays on electrified bodies, 211, 245
 new properties of X rays, 74, 280
- Bentley, W. H., E. Haworth, and W. H. Perkin, jun., derivatives of phenoxyethylmalonic acid, 104
 W. H. Perkin, jun., and J. F. Thorpe, cis- and trans-methylisopropylsuccinic acids, 152
 xylic and xylidinic acid, 208
 Benzene nucleus, 59
 solubility in water of certain substitution derivatives, 153
 Benzidine and tolidine, valuation of, 275
 Berthelot's contributions to the history of chemistry, 214
 Bernard, J., and R. Engel, determination of arsenic, 121
 Bertrand, G., new oxidase, 293
 Besançon, A., photographic proofs obtained in darkness, 119
 Bessemer or open-hearth steels, cemented, 192
 Besson, A., action of carbonyl chloride, 83
 action of gaseous hydriodic acid, 293
 of hydrobromic acid, 221
 of hydrobromic gas, 257
 Bettelheim, D. A., "Spiritual Heroes, a Collection of Biographies" (review), 21
 Bevan, E. J., C. Smith, and C. F. Cross, constitution of the cereal celluloses, 228
 Birnbaum, K., P. A. Bolley, C. Engler, and F. Fischer, "Handbook of Chemical Technology" (review), 256
 "Black light," condensation of, 269
 "Bleaching and Calico Printing" (review), 58
 Blende, hexagonal, as a substitute for Crookes phials, 143
 Bleunard and Labesse, MM., passage of Röntgen rays through liquids, 133
 resistance of some liquids and solids to X rays, 177
 Blount, B., and A. G. Bloxam, "Chemistry for Engineers and Manufacturers" (review), 94
 Bloxam, A. G., and B. Blount, "Chemistry for Engineers and Manufacturers" (review), 94
 Blythe, G. W., preparation of pure anhydrous hydrocyanic acid, 71
 Blyth, A. W., "Foods; their Composition and Analysis" (review), 244
 Bolley, P. A., K. Birnbaum, C. Engler, and F. Fischer, "Handbook of Chemical Technology" (review), 256
 Bolton, H. C., Berthelot's contribution to the history of chemistry, 214
 Bone, W. A., and D. S. Jordan, union of carbon and hydrogen, 151
 and W. H. Perkin, jun., dimethylglutaric acids, 152
 symmetrical dimethyl succinic acids, 152
 Bordas, F., and C. Girard, Röntgen rays, 163
 Borgmann, J. J., and A. L. Gerchun, action of Röntgen rays, 110
 Boric acid in nature, 12
 apparatus for the detection of, 230
 Boride, nickel, and cobalt, 141
 Boron bronze, 262
 Bouchardat, G., and M. Tardy, Russian aniseed oil, 95, 164
 Boudouard, O., and P. Schutzenberger, earths contained in monazite sands, 202
 Bourquelot, E., hydrolysing ferment of gaultheria, 257
 Bouveault, L., action of ethyl-oxalyl chloride, 269
- Bouveault, L., and P. Barbier, extraction of rhodinol, 153
 rhodinol, 166
 synthesis of geranic acid, 119
 Boyle lecture, the, 283
 Bran and lime, experiments with, 106
 British Imperial Exhibition at Montreal, 131
 Brochet, A., action of the halogens on ferric aldehyd, 48
 Bromine, crystallisation of, 197
 heat value of oils and fats, 87
 Bromocamphor, 207
 Bromocamphorsulphonic acid, oxidation products of, 208
 Bronze, boron, 262
 Brooks, O. J., quantitative estimation of tin, 218
 Brühl, J. W., constitution of water, 26
 Brullé, K., determination of the purity of butter, 119
 Building Materials Congress, 83
 Buisine, M., manufacture of hydrochloric acid, 258
 Buguet, A., and A. Gascard, action of X rays on the diamond, 121
 action of X rays on precious stones, 186
 Burrell, B. A., analysis of water from the dropping well at Knaresborough, 196
 Burette, new, 281
 Butter, determination of the purity, 119
 Butterfield, W. J. A., "Gas Manufacture" (review), 21
- CAIN, J. C., action of hydrogen chloride, 82**
 "Calico Printing and Bleaching" (review), 59
 Calmette, L., and G. T. Huillier, diffraction of the Röntgen rays, 212
 Cameron, C. A., "Elementary Agricultural Chemistry and Zoology" (review), 93
 Campbell, M., direct measurement of the electric current, 255
 measurement of alternating currents, 290
 E. D., oxidation of some gases with palladised copper oxide, 32, 52, 78
 and E. B. Hart, quantitative determination of hydrogen, 274
 Campholenic derivatives, 95
 Campholide, 119
 Camphoric acid derivatives, 267
 Canichel, C., and M. Bayrac, absorption of light, 95
 Carbide, manganese, 141
 uranium, 118
 Carbides of yttria and thoria, 164
 Carbon and hydrogen, union of, 151
 dioxide, 252
 formation, 139
 monosulphide, experiments for the production of, 23
 "Carbohydrates, Physiology of" (review), 34
 Carbohydrates, transformation of fat into in certain animals, 280
 Carbonyl chloride, action, 83
 Carnegie, D., and H. Wales, volumetric composition of ammonium chloride, 26
 Carnot, A., volumetric analysis of a mixture of chlorides, hypochlorides, and chlorates, 157, 169
 Carpentier, J., photograph in relief with Röntgen rays, 155
 Carr, F. H., and W. R. Dunstan, determination of nitrogen, 128
 Causse, H., phenylhydrazine tartrate, 245
 Cazeneuve, P., preparation of glyceric acid, 293
- Cebo, K., and K. Schmitz, production of pinacones, 153
 Cell, new storage, 191
 Cellulose, increase in the temperature of, 180
 Cemented open-hearth or Bessemer steels, 192
 Ceramic stones from the devitrification of glass, 306
 Cereal celluloses, constitution, 228
 Chabaud, V., permeability of metals for the X rays, 85
 specimens of glass exposed to the action of X rays, 143
 Chapman, E. T., and J. A. Wanklyn, "Water Analysis" (review), 196
 Chappuis, J., and E. Nuges, condition of the maximum of power of Crookes tubes, 202
 Charas, 207
 Charpy, G., structure and constitution of alloys of copper and zinc, 168
 Charrin and D'Arsonval, MM., action of currents of high frequency on bacterial toxins, 119
 Chattaway, F. D., and R. C. T. Evans, metadichlorobenzene, 229
 metadiphenylbenzene, 266
 Chaveau, A., source and nature of the potential directly utilised in muscular work, 293, 305
 transformation of fat into carbohydrate in certain animals, 280
 Chemical and atmospheric nitrogen, combination with metals, 115
 Institute of Kiel University, 59, 107, 175
 laboratory of Wiesbaden, 131
 researches and spectroscopic studies, 5, 15, 29, 39, 51, 66, 80, 83, 113, 124, 135, 147, 159, 171, 183, 192, 204, 216, 224, 241, 249, 263
 Society, 9, 40, 53, 68, 81, 91, 103, 126, 138, 159, 194, 206, 229, 225, 252, 266, 291, 301
 Edinburgh University, 56, 117
 "Chemical Elements, True Atomic Weights of the" (review), 231
 "Chemical Experiments" (review), 280
 "Chemical Novelties, &c." (review), 209
 "Chemical Solubilities, Dictionary" (review), 278
 "Chemical Technology, Handbook of" (review), 256
 Chemically pure CS₂, 6
 "Chemico-organic Compounds, Book of Tables of" (review), 293
 "Chemistry and Zoology, Elementary Agricultural" (review), 93
 "Chemistry, Elementary Practical" (review), 196
 "Chemistry for Engineers and Manufacturers" (review), 94
 "Chemistry in Daily Life" (review), 303
 "Chemistry, Manual of Inorganic" (review), 46
 "Chemistry of Pottery" (review), 46
 "Chemistry, Practical Inorganic" (review), 34
 "Chemistry, Service" (review), 10
 Chemistry, Berthelot's contribution to the history of, 214
 of dibromopropylthiocarbimide, 9
 of the cyanide process for dissolving gold, 272
 "Chemists and Druggists, Kelly's Directory of" (review), 303
 "Chemists, Machinery and Appliances for" (review), 37
 Chesneau, M., temperature of uranium spark, 142

- Chevalier and Gossart, M.M., mechanical action emanating from the Crookes tube analogous to the photographic action discovered by Röntgen, 98
- Chloraloses, 281
- Chloride, ethylxalyl, action of, 269
- ferrie, action of, 24
- of hydrogen, action of, 82
- Chlorides, &c., volumetric analysis of a mixture, 157, 169
- of zirconium, 25
- Chlorine, conversion into hydrochloric acid, 197
- peroxide, explosion of, 139
- Chlorocarbonic oxide, action of, 17
- Chloronitrocamphor, decomposition of, 207
- "Chlorophyll, Chemistry of" (review), 23
- Chloroplatinates, determination of, 87
- Chrome iron ore, ferro-chromium, and chrome steel, analysis of, 1
- Chromium sulphide, crystalline properties of, 35
- Chromous carbonate, crystalline ammoniacal, 142
- City and Guilds of London, 120
- "City and Guilds of London, Report" (review), 279
- Clever, A., and W. Muthmann, compounds of selenium with arsenic, 198
- Clothing, microscopic structure of, 281
- "Club Reprints, Alembic" (review), 245
- Coal, arsenic in, 191
- calculation of the thermic power of, 91
- ash, composition and fusibility of, 59
- mounds and the hardness of water, 59
- Cobalt, new compound of, 228
- Cohen, J. B., and W. H. Archdeacon, action of sodium alcoholate, 81
- Cohn, L., and M. M. P. Muir, "Chemistry in Daily Life" (review), 303
- Collie, J. N., and W. Ramsay, helium and argon, 259
- and N. T. M. Wislome, production of naphthalene derivatives, 128
- Colloidal compounds of the rare metals, 284
- Colour of ions as a function of the atomic weight, 198, 221
- origin of, 126
- photography, 213
- Colson, A., synthesis of hydrochlorates of amides, 43
- R., action of X rays on photographic plates, 245
- photography through opaque bodies, 144
- Corney, A. M., "Dictionary of Chemical Solubilities" (review), 278
- Condensation products, quantitative determination of, 23
- Copper and arsenic, separation of mercury from, 28, 38
- and manganese cyanides, 24
- and zinc alloys, 168
- iron, magnesium, &c., combination of atmospheric nitrogen with, 35
- metallurgy and analysis, 117
- oxide, oxidation of some gases with palladinised, 22, 52, 78
- silicide, 119
- Coppock, J. B., existence of cupric sulphide, 262
- Coquillion, J., modifications of the methanometer, 164
- Coreil, F., "L'Eau Potable" (review), 46
- Cotton oil in American lards, 83
- Cresol, value of crude, 169
- Crookes, W., and J. Dewar, London water supply, 5, 65, 111, 146, 193, 241, 300
- phials, hexagonal blends as a substitute, 143
- Crookes tube of a spherical form showing the reflection of the kathode rays by the glass and the metal, 72
- mechanical action emanating from, analogous to the photographic action discovered by Röntgen, 98, 197, 211
- photography in the interior of, 232
- tubes, condition of maximum of power of, 202
- heterogeneity of the radiations emitted by, 245
- mechanical action emanating from, 178, 197
- penetration of gases into the glass sides of, 198
- Cross, C. F., E. J. Bevan, and O. Smith, constitution of the cereal celluloses, 228
- Crystalline and liquid states, substances which exhibit rotatory power in both, 267
- tin sulphophosphide, 119
- Cupric sulphide, existence of, 262
- Cupellation of metals, 282
- Currents, measurements of alternating, 290
- Curtius, T., glycol hydrazid, 59
- Cushman, A. S., and J. Hayes-Campbell, volumetric determination of lead, 90
- Cyanacetates, action of, 233
- Cyanide process, chemistry of, 272
- "Cyanide Processes" (review), 118
- Cyanogen, explosion of, 138
- Cylinders, composition of flours by grinding hard and soft wheats in, 35
- D'ABBADIE, M., immunity against bites of serpents, 142
- D'Arcy, R. F., sodium sulphate, 252
- D'Arsonval, A., photography through opaque substances, 133
- and M. Charrin, action of currents of high frequency on bacterian toxins, 119
- Dahl, O. W., and C. Beadle, increase in the temperature of cellulose, 180
- Daniel, J., mechanical action emanating from the Crookes tube, 197
- Dareste, G., influence of electricity on the embryo of the fowl, 36
- Dastre, A., solubility and activity of soluble ferments in alcoholic liquids, 12
- De Bruyn, C. A. L., free hydrazin, 86
- hydrazin hydrate, 86
- De Coninck, O., isomerism in the aromatic series, 186
- De Heen, M., X rays emanate from the anode, 119
- De Karnojitzsky, M., and Prince B. Galitzin, centres of emission of the X rays, 164
- Delépine, M., methylamine, 305
- De Metz, G., photography in the interior of the Crookes tube, 232
- De Rey-Pailhade, J., respective roles of phlothin and lacase in seeds during germination, 48
- De Wylde, B., extraction of gold from tailings, &c., 95
- Deeley, R. M., helium and the gas X, 13
- Dehéralin, P. P., and M. Demoussy, circulation of air in the soil, 72
- fallows, 221
- Delafontaine, M. M., some colloidal compounds of the rare metals, 284
- Demarçay, E., new element in the rare earths contiguous to samarium, 170
- Demoussy, M., and P. P. Dehéralin, circulation of air in the soil, 72
- Denigès, G., detection of mercury and iodides, 134
- three new reagents for nitrites, 27
- Denninger, A., experiments for the production of carbon monosulphide, 23
- "Dentists' Register" (review), 185
- Deslandres, H., absorption of nitrogen by cold lithium, 12
- Desylene acetic acid, 254
- Dewar, J., liquefaction of air and research at low temperatures, 40
- and W. Crookes, London water supply, 5, 65, 111, 146, 193, 241, 300
- Diamond, action of X rays on, 121
- Diazomides, mixed, 129
- Diazobenzene compounds, constitution of, 107
- Dibenzoylglyceric acid, &c., some of the etheral salts of active and inactive, 81
- Dibromopropylthiocarbamide, chemistry of, 9
- Dielecrica, 255
- Dimethoxydiphenylmethane, and some derivatives, 268
- Dimethylaniline, derivatives of, 53
- Dimethylglutaric acids, 152
- Diphenyl di-isocyanate, action on amido-compounds, 37
- Dithiazolic derivatives, certain, 43
- Dixon, A. E., acidic thiocarbides, thioureas, and ureas, 230
- chemistry of dibromopropylthiocarbamide, 9
- halogen additive products of substituted thiosinnamines, 229
- H. B., formation of carbon dioxide, 139
- and J. A. Harker, explosion of chlorine peroxide, 139
- E. H. Strange, and E. Graham, explosion of cyanogen, 138
- Dobriner, P., and W. Schranz, determination of moisture in aniline, 270
- determination of aniline, 236
- Doherty, W. M., apparatus for the detection of boric acid, 230
- arsenic in coal, 191
- Doran, R. E., action of lead thiocyanate, 206
- Dresden, researches from the organic laboratories of the Technical High School, 23
- "Druggists and Chemists, Kelly's Directory of" (review), 303
- Duclaux, E., industrial work of Pasteur, 258
- Duerf, G., and W. Turnbull, "Bleaching and Calico Printing" (review), 58
- Dufau, E., crystalline barium tetrachromite, 281
- Dufour, H., proofs obtained by Röntgen's procedures, 62
- Dunstan, Prof. Wyndham R., appointment at the Imperial Institute, 175
- and F. H. Carr, determination of nitrogen, 128
- E. Goulding, hydriodides of hydroxylamine, 196
- Dupont, J., cotton oil in American lards, 83
- Durrant, R. G., new compound of cobalt, 228
- EASTERFIELD, T. H., W. T. N. Spivey, and T. B. Wood, charas, 207
- Edinburgh University Chemical Society, 56, 117
- Edison effect, the, 162
- Edwards, A. M., solubility of silica, 13
- V., rapid estimation of insoluble phosphate, 25, 71
- Electric arc, true resistance of, 243
- currents, direct measurement of, 255
- strata, action of Röntgen rays on double and triple, 223
- "Electrical Literature, Synopsis of Current" (review), 256
- phenomena produced by Röntgen rays, 109
- science, researches placed at the service of medicine and surgery by, 131
- "Electricity and Gas, Comparative Cost in Chili" (review), 221
- influence on the embryo of the fowl, 36
- of metals, effect of X rays on the contact, 165
- Electrified bodies, action of X rays on, 211, 232, 245
- Röntgen rays, 189, 223, 232, 245
- Electro-dissolution, its uses, 37
- Electrolyser, new, 280
- Electrolysis of potassium allo-ethylis camphorate, 254
- sodium in aluminium prepared by, 64
- Electrometric determination of the final point in volumetry, 270
- Electrostatic deflection of the kathode rays, 257
- Element, new, in rare earths contiguous to samarium, 170
- Elements, argon and helium in the system of, 235
- numerical relations in the atomic weights of, 203
- place of helium in the classification of, 23, 35, 283
- thallium in relation to the genesis of, 304
- Emerald, treatment of the, 3
- Engel, K., and J. Bernard, determination of arsenic, 121
- Engels, C., preliminary communication, 24
- Engler, C., F. Fischer, P. A. Boiley, and K. Birnbaum, "Handbook of Chemical Technology" (review), 256
- "Engineers and Manufacturers, Chemistry" (review), 94
- Errera, L., action of X rays upon a phycmyces, 210
- Esters, substituted glycolic, 59
- Etard, M., and H. Moissan, yttrium and thorium carbides, 164
- Ether, generation of longitudinal waves in, 112
- Etherification, note on, 127
- Ethyl aceto-acetate, 196
- Eumorphopoulos, M., and W. Ramsay, determination of high temperatures by the maldometer, 93
- Evans, Miss O. de B., derivatives of dimethylaniline, 53
- P. S., jun., and F. A., Gooch, reduction of selenic acid, 273
- R. C. T., and F. D. Chattaway, metadichlorobenzene, 229
- metadiiphenylbenzene, 266
- Everett, J. D., resultant tones, 56
- Ewan, T., electrolytic conductivity of formamide and thioformamide, 81
- Exhibition, British Imperial, at Montreal, 131
- "Explosives Acts" (review), 292
- "FACTORY Acts, The" (review), 34
- Fallows, 221
- Fatty foods, immediate destination, 293

- Fatty series, distillation of the first acids of, 245
 Fats and oils, bromine heat value of, 87
 Favrel, G., action of cyanacetates, 233
 Fenton, H. J. H., constitution of a new organic acid, 194
 Ferée, J., amalgams of molybdenum, 186
 "Fermentation, Practical Studies in" (review), 118
 Ferments soluble in alcoholic liquids, solubility and activity of, 12
 Ferrand, M., new series of sulphophosphides, 233
 sulphophosphides, 156
 Ferric chloride, action of, 24
 Ferro-chromium analysis, 1
 Ferrocyanides, 24
 Filetti, M., and G. Ponzo, conversion of ketones into diketones, 107
 Filsinger, F., detection of Tus-sah silk in textile goods, 236
 Fire-damp, composition of, 119
 Fischer, E., and A. Kling, "Exercises in the Preparation of Organic Compounds" (review), 22
 F., P. A. Bolley, K. Birnbaum, and C. Engler, "Handbook of Chemical Technology" (review), 256
 Fitzgerald, G. F., Helmholtz memorial lecture, 91
 Flame, our knowledge of, 197
 Flames, temperature of, 229
 Flammarion, C., action of various radiations of the solar spectrum on plants, 36
 Fleming, J. A., Edison effect, 162
 Prof. and M. Peteval, analytical study of the alternating current arc, 116
 Flours, composition by grinding hard and soft wheats in cylinders, 35
 Fluorene and acenaphthalene, 254
 Fluorides of acids, 107
 Fluor spar, 306
 Fontana, A., and A. Umani, mechanical action emanating from Crookes tubes, 211
 "Food and Sanitation" (review), 141
 "Foods, their Composition and Analysis" (review), 244
 Formaldehyd, conversion of the solution of liquid, 142
 Formanilide and thioformanilide, electrolytic conductivity of, 81
 Formic aldehyd, action of the halogens, 48
 Fowl, influence of electricity on the embryo of, 36
 François, M., action of alcohol on mercurous iodide, 12
 of heat on mercurous iodide, 95
 Frankland, E., past, present, and future water supply of London, 99
 P., and J. MacGregor, some of the etheral salts of active and inactive dibenzoyl glyceric acid, &c., 81
 R. H. Picard, rotation of optically active compounds, 82
 Freiburg University Laboratory, researches, 23, 29, 107, 153
 Fresenius, K., and E. Hintz, peculiar relations of solubility of barium sulphate, 276
 Friedrich, and Greiner, MM., new burette, 281
 Frith, J., effect of wave-form on the alternate current arc, 209
 and Rogers, Messrs., true resistance of the electric arc, 243
 Fromon, O., and F. Mylius, production of pure zinc, 24
 Frye, C. C., oxidising substance by distilling aqueous solutions of potassium permanganate and sulphuric acid in vacuo, 122
 GAAB, K., and K. Seubert, action of ferric chloride, 24
 Galitzin, Prince B., and M. de Karnojitzky, centres of emission of the X rays, 164
 Garbassa, A., and A. Batelli, some facts relating to Röntgen rays, 164
 Garhey, M., ceramic stones obtained by the devitrification of glass, 306
 Gas, action of hydrobromic, 257
 analytical apparatus, 158
 from the Bath springs, argon and helium in, 247
 prolonged action of low heating on detonating, 18
 X and helium, 13
 "Gas Manufacture" (review), 21
 "Gas and Electricity, Comparative Cost in Chile" (review), 221
 Gascard, A., and A. Buguet, action of X rays on the diamond, 121
 on precious stones, 186
 Gaseous combinations, some conditions which govern, 164
 Gases of different densities, acoustic analysis of mixtures of, 47
 penetration of into the glass sides of Crookes tubes, 198
 Gassmann, C., peridinon-naphthalene, 245
 Gaultheria, hydrolysing ferment of, 257
 Gautier, A., determination of arsenic, 134
 and H. Helier, some conditions which govern gaseous combinations, 164
 Genesis of the elements, thallium in relation to, 304
 Geometrical instruments, 56
 Geranic acid, synthesis of, 119
 Gérard, E., fermentation of uric acid, 257
 researches placed at the service of medicine and surgery by electrical science, 131
 Gerchun, A. L., and J. J. Bergman, action of Röntgen rays, 110
 German naturalists and physicians, meeting of, 185
 Gernez, G., rotatory property of superfluid rhannose, 48
 Girard, A., composition of flours by grinding hard and soft wheat in cylinders, 35
 C., and F. Bordas, Röntgen rays, 163
 Girardet, F., and M. Meslans, fluorides of acids, 107
 Gladstone, J. H., place of helium in the classification of elements, 23
 Glaser, C., volumetric determination of phosphoric acid, 212
 Glass, action of alumina, in the composition of, 175
 ceramic stones from the denitrification of, 306
 exposed to the action of the X rays, 143
 remarkable change in the structure by heating, 48
 Glucina, preparation of pure, 3
 Glyceric acid, preparation of, 293
 Glycoccine, constitution of, 106
 Glycol, 105
 Glycolic esters, substituted, 59
 Gold, extraction from tailings, &c., 95
 presence of, in silver ores, 71
 Gooch, F. A., and P. S. Evans, jun., reduction of selenic acid, 273
 W. S. Scoville, reduction of selenic acid, 285
 Gossart and Chevalier, MM., mechanical action emanating from the Crookes tube analogous to the photographic action discovered by Röntgen, 98
 Goudet, C., and P. A. Guye, optical superposition of six asymmetric carbons in the same active molecule, 245
 Goulding, E., and W. R. Dunstan, hydriodides of hydroxylamine, 196
 Gouy, M., refraction of X rays, 293
 penetration of gases into the glass sides of Crookes tubes, 198
 Goyder, G. A., chemistry of the cyanide process for dissolving gold, 272
 Graham, E., E. H. Strange, and H. B. Dixon, explosion of cyanogen, 138
 Granger, A., crystalline iron sesquiphosphide, 245
 tin sulphophosphide, 119
 Graphite in pig-iron, determination of, 31
 Gréhan, M., explosive mixtures of acetylene and air, 222
 Greiner and Friedrich, MM., burette with specular black wall, 281
 "Guilds of London, and City, Report" (review), 279
 Gunz, M., lithium hydride, 167
 subchloride, 35
 properties of metals extracted from their amalgams, 138
 Guye, P. A., and C. Gaudet, optical superposition of six asymmetric carbons in the same active molecule, 245
 HAKE, H. W., absorption of moisture by deliquescent salts, 104
 Haller, A., campholide, 119
 extraction of terpenic alcohols, 232
 Halogens, action on formic aldehyd, 48
 determination of, 281
 Hanmann, J., determination of phosphoric acid, 53
 Hanriot, M., chloraloses, 281
 Hansen, E. C., and A. K. Miller, "Practical Studies in Fermentation" (review), 118
 Hardy, E., acoustic analysis of mixtures of two gases of different densities, 47
 Harker, J. A., and H. B. Dixon, explosion of chlorine peroxide, 139
 Hart, E. B., and E. D. Campbell, quantitative determination of hydrogen, 274
 Hartley, W. N., composition of a white sou, 229
 temperature of flames, 229
 Haworth, E., and W. H. Perkin, jun., glycol, 105
 and W. H. Bentley, derivatives of phenoxethylmalonic acid, 194
 Hayes-Campbell, J., and A. Cushman, volumetric determination of lead, 90
 "Health and Beauty, Helps to" (review), 34
 Heating, remarkable change in the structure of glass by, 48
 Hébert, A., and G. Truffaut, physiological study of Persian cyclamens, 291
 Helier, H., and A. Gautier, some conditions which govern gaseous combinations, 164
 Helium and argon, 259
 further details, 56
 in the gas from the Bath springs, 247
 in the system of the elements, 235
 Helium, some physical properties of, 75
 and the gas X, 13
 line D₃, wave-length, 14
 in place of in the classification of elements, 23, 35, 283
 Helmholtz memorial lecture, 91
 Henderson, J., action of sugar on ammoniacal silver nitrate, 81
 and J. Walker, electrolysis of potassium allo-ethylic camphorate, 254
 Henry, C., increase of the photographic yield of the Röntgen rays, 98
 principle of an accumulator of light, 175
 "Heroes, Spiritual" (review), 27
 Hinds, J. I. D., quantitative determination of lime and sulphuric acid, 285, 299
 Hinrichs, G. D., "True Atomic Weights of the Chemical Elements" (review), 231
 Hintz, E., and R. Fresenius, peculiar relations of solubility of barium sulphate, 276
 Hodgkinson, W. R., fluorene and acenaphthalene, 254
 Holloway, G. T., and B. Redwood, "Petroleum" (review), 130
 Holman, S. W., "Computation Rules and Logarithms" (review), 107
 Horse sickness of South Africa, 246
 Humphreys, W. J., solution and diffusion of certain metals in mercury, 81
 Hutchinson, A., and W. Pollard, lead tetracetate, and plumbic salts, 103
 Huillier, G. T., and L. Calmette, diffraction of the Röntgen rays, 212
 Hurion and Izarn, MM., deviation of the X rays by a prism, 293
 Hurmuzescu, D., and L. Benoist, action of X rays on electrified bodies, 211, 245
 new properties of X rays, 74, 280
 Hydratin, free, 86
 hydrate, production of certain properties, 86
 Hydrindone derivatives, 9
 Hydriodic acid, action of gaseous, 293
 Hydriodides and hydroxylamine, 196
 Hydrobromic acid, action of, 221
 gas, action of, 257
 Hydrochlorates of amides, synthesis of, 48
 Hydrochloric acid, manufacture of, 258
 Hydrocyanic acid, preparation of pure anhydrous, 71
 Hydrogen and carbon, union of, 151
 chloride, action of, 82
 liquefaction of, 219
 peroxide, specific heat of, 24
 quantitative determination of, 274
 the proper place for, 283, 305
 IMBERT, A., and H. Bertin-Sans, diffusion of Röntgen rays, 155
 radiographs, 257
 stereoscopic photographs with X rays, 210
 Indicators, a study of, 287
 Industries, Trades, and Arts Exhibition, 149
 "Inorganic Chemistry, Manual" (review), 46
 "Inorganic Chemistry, Practical" (review), 34
 Institute, Iron and Steel, 198
 Institution, Royal, 119, 142, 175, 199, 246, 284
 "Intensity Coils, How Made and How Used" (review), 141

- Iodide, action of heat on mercurous, 95
 Iodides and mercury, detection, 134
 Ions, atoms, and molecules, relations of the colours of, 43, 260, 271
 colour of as a function of the atomic weights, 23, 198, 221
 Iron and Steel Institute, 198
 and tannic acid in ores, determination, 123
 colorimetric determination of, 250
 nitrosulphides, 72
 sesquiphosphide, crystalline, 245
 Isomerism in the aromatic series, 186
 Izarn and Hurion, MM., deviation of X rays by a prism, 293
- JACKSON, H.**, phosphorescent substances in rendering X rays visible, 150
Jannasch, P., and **K. Aschoff**, determination of the halogens, 281
 and **E. Rose**, separation of metals in a current of carbonic acid charged with bromine, 24
Japp, F. R., and **G. D. Lander**, reduction of desyleneacetic acid, 254
 synthesis of pentacarbon rings, 253
Jaubert, G. F., novel salranines, 35
Jaumann, G., electrostatic deflection of the cathodic rays, 257
Jay, H., distribution of boric acid in nature, 12
Jean, F., and **G. Mercier**, "Reperatory of Special Reagents" (review), 163
Jones, V., method of finding the true value of the ohm, 255
Jordan, D. S., and **W. A. Bone**, union of carbon and hydrogen, 151
- KATHODE** rays, 61, 140
 reflection by glass and metal, a Crookes's tube of a spherical form, 72
 Kathodic rays, electrostatic deflection of the, 257
Kebler, L. F., acidimetric estimation of vegetable alkaloids, 287, 298
 "Kelly's Directory of Chemists and Druggists" (review), 303
 "Kelly's London Medical Directory" (review), 106
Kelvin Bridge, adjustment of, 208
Lord, generation of longitudinal waves in ether, 112
Kern, S., casting of steel, 88
 cemented open-hearth or Bessemer steels, 192
 production of steel for steel castings, 179
 the Walrand-Légénis process for steel castings, 111, 179
Kerr, M., paraffin industry, 56
 Ketones into diketones, conversion of, 107, 153
Kiel University, Chemical Institute of, 59, 107, 175
Kipping, F. S., derivatives of camphoric acid, 267
 and **A. Lapworth**, oxidation products of bromocamphor sulphonic acid, 208
 and **C. Revis**, derivatives of hydriodone, 9
 bromocamphor, 207
Kling, A., and **E. Fischer**, "Exercises in the preparation of Organic Compounds" (review), 22
Klein, A., and **A. Werner**, so-called amido-chromates, 48
- Knowles and Ackroyd, Messrs.**, permeability to Röntgen rays, 140
Kreichgauer, A., quantitative determination of lead, 24
Kreider, D. A., preparation of perchloric acid, 8, 17
Kurnakow, N., complex metallic bases, 23
- LABESSE and Bleunard, MM.**, passage of Röntgen rays through liquids, 133
 resistance of some liquids and solids to X rays, 177
 "Laboratory Tables for Qualitative Analysis" (review), 163
 Laccase and phloethion, respective roles of in seeds during germination, 48
Landauer, J., "Spectrum Analysis" (review), 70
Lander, G. D., and **F. R. Japp**, reduction of desyleneacetic acid, 254
 synthesis of pentacarbon rings, 253
Langenbeck, K., "Chemistry of Pottery" (review), 46
Lannelongue and Oudin, MM., application of Röntgen rays in surgical diagnosis, 97
 and **Barthelemy, MM.**, utility of photographs in human pathology taken with X rays, 61, 186
Lapworth, A., decomposition of chloronitrocamphor, 207
 and **F. S. Kipping**, oxidation products of bromocamphor sulphonic acid, 208
Lards, cotton oil in American, 83
Lascelles, B. P., "Single Salt Analysis" (review), 163
Lauth, C., certain dithioazolic derivatives, 48
Law, R., auxiliary assay balance, 207
Laycock, W. F., experiments with bran and lime, 106
Les, C., numerical relations in the atomic weights of the elements, 203
 relations of the colours of atoms, ions, and molecules, 48, 260, 271
Lead analysis, volumetric method for, 18
 quantitative determination of, 24
 tetracetate, 103
 thiocyanate, action of, 206
 tin, &c., analysis of alloys, 25
 volumetric determination of, 90
Leather industries, 24
Leaves, yellow autumnal matter of, 86
Lebeau, P., treatment of the emerald, 3
Le Bon, G., photography with dark light, 73, 110, 121, 133, 269
Le Chatelier, H., combustion of acetylene, 47
 formation heat of some compounds of manganese, 59
 report on recent work of Richards on aluminium, 306
Le Roux, F., heterogeneity of the radiations emitted by Crookes tubes, 245
Lefay, A., deflection of Röntgen rays by magnets, 177, 189
 Röntgen rays electrified, 189, 223, 232, 245
Lehfeldt, R. A., symbolism in thermodynamics, 208
Lengfeld, M., and **H. Moissan**, new zirconium carbide, 175
Leon, F., nitric acid, detection of, 251
Lévy, L., crystalline titanium, 47
Lewes, V. B., acetylene, theory of luminosity, 68
 "Service Chemistry" (review), 10
- Light**, absorption of, 95
 and water, action of in liberating the perfumes of plants, 164
 photography with dark, 73, 74, 110, 121, 133, 269
 principle of an accumulator, 175
 "Light, The Old and the New" (review), 293
Lime and sulphuric acid, quantitative determination of, 285, 299
Linb, C., possibility of separating atmospheric argon and nitrogen, 24
Lindot, L., identification of principal acids in plants, 295
Lippmann, G., colour photography by the interferential method, 213
 Liquids and solids, resistance of some to Röntgen rays, 177
 passage of Röntgen rays through, 133
Lithium, cold, absorption of nitrogen by, 12
 hydride, 107
 subchloride, 35
Litmus pencils, 198
"Logarithms, Computation Rules and" (review), 107
Londe, A., application of Röntgen's method, 97
 "London, City and Guilds, Report" (review), 279
London, City and Guilds of, 120
 water supply, 5, 65, 111, 146, 193, 241, 300
 past, present, and future, 99
Long, J. H., inversion of sugar by salts, 161, 173
 Longitudinal waves in ether, generation of, 112
Lorenz, R., conversion of chlorine into hydrochloric acid, 197
Lorlet, L., influence of induction currents on the orientation of living bacteria, 233
Lumière, A. and L., photographic researches on Röntgen rays, 155
Luminosity, acetylene theory, 68
Lunge, G., colorimetric determination of iron, 250
 "Manufacture of Sulphuric Acid and Alkali" (review), 268
Luteol, 62
Luteolin, 105, 252
- MACGREGOR, J.**, and **P. Frankland**, some of the ethereal salts of active and inactive dibenzoyl glyceric acid, &c., 81
Mackenzie, J. E., dimethoxydiphenylmethane, 268
 metallurgy and analysis of copper, 117
Magnesium, aluminium, iron, copper, &c., combination of atmospheric nitrogen with, 35
 Magnetic rotatory power of aromatic compounds, 301
Magnets, deflection of Röntgen rays by, 177, 189
Maize, 257
Malic and lactic acids, ethereal salts of optically active, 229
Maltézos, C., certain properties of X rays, 280
Manganese and copper cyanides, 24
Manganese carbide, 141
 formation heat of some compounds of, 59
Maquenne, L., fixation of nitrogen, 47
Marchetti, G., certain potassium fluorides and oxyfluorides, 197
Marchlewski, L., "Chemistry of Chlorophyll" (review), 23
Marey's, M., official visit to the Royal Society, 11
- Marie, C.**, and **R. Marquis**, iron nitrosulphides, 72
 new method of forming nitroprussides, 142
Marpmann, M., colouration of sausages, 281
Marquis, R., and **C. Marie**, new method of forming nitroprussides, 142
Mason, W. P., examination of potable water, 237
 "Water Supply" (review), 304
P., water evaporation, 281
Massol, G., melting and solidification points of some acids of the fatty series, 65
O., the proper place of hydrogen, 283
Mathiessen's standard, exact value of, 140
 "Medical Register" (review), 185
Medicine and surgery, researches placed at the service of by electrical science, 131
Meldola, R., mononitroguaiacol, 302
 and **E. R. Andrews**, alkaline reduction of metanitriline, 9
 and **F. W. Sreatfield**, mixed diazoamide, 129
 relations between melting-point and constitution, 130
Meldometer, determination of high temperatures by, 93
 Melting-point and constitution, relation between, 130
Mercier, G., and **F. Jean**, "Reperatory of Special Reagents" (review), 163
Merck, E., "Annual Report for 1895" (review), 280
 molybdic acid as a reagent for alcohol, 149
Mercuric salts, determination of, 198
Mercurous iodide, action of alcohol on, 12
 of heat on, 95
 salts, 83
Mercury and iodides, detection, 134
 separation from arsenic and copper, 28, 38
 solution and diffusion of certain metals in, 81
Meslans, M., permeability of metals to the Röntgen rays, 97
 and **F. Girardet**, fluorides of acids, 107
Meslin, G., use of non-uniform magnetic fields in photography with X rays, 189
Mesnard, E., action of light and water in liberating the perfumes of plants, 164
Messner, J., ferrocyanides, 24
Metadichlorobenzene, 229
Metadiiphenylbenzene, 266
Metanitriline, alkaline reduction of, 9
Metallic bases, complex, 23
 objects, photography of through opaque substances, 85, 133, 144
 uranium, new radiations by, 295
Metals, combination of atmospheric and chemical nitrogen with, 115
 direct combination of the nitrogen of the atmosphere to, 62
 effect of X rays on the contact electricity, 165
 extracted from their amalgams, properties of, 138
 noble, law of during cupellation, 282
 permeability of for X rays, 85, 97, 155
 separation of, 24
 some colloidal compounds of the rare, 284
 volumetric determination of, 247, 277
Metallurgy and analysis of copper, 117

- "Metallurgy, Manual of" (review), 22
- Methanometer, modifications of, 164
- Methylamines, 305
- Methylisopropylsuccinic acids, cis- and trans-, 152
- Meunier, J., dichloralglucose in monochloralglucosane, 83
- Meyer, V., fusibility of platinum, 235
- and W. Raum, prolonged action of low heating on detonating gas, 18
- Mica merchants, F. Wiggins and Sons, new address, 7
- Miller, A. K., and E. C. Hansen, "Practical Studies in Fermentation" (review), 118
- Mitchell, W. L., and H. L. Wells, determination of titanous acid and iron in ores, 123
- Moissan, H., analysis of aluminium and its alloys, 49
- manganese carbide, 141
- nickel and cobalt boride, 141
- properties of uranium, 296
- sodium in aluminium prepared by electrolysis, 64
- uranium carbide, 118
- and M. Etard, yttrium and thorium carbides, 164
- and M. Lengfeld, new zirconium carbide, 175
- Mola, P., toxicological detection of aqua regia, 27
- Molecular volume of organic substances in solution, 54
- weight of phosphoric anhydride, 103
- "Molecular Weight, Guide to the Determination of" (review), 58
- Molecule, active optical, superposition of six asymmetric carbons in the same, 245
- "Molecules and the Molecular Theory of Matter" (review), 34
- Molecules, atoms, and ions, relations of the colours of, 48, 260, 271
- Molybdenum amalgams, 186
- Molybdic acid as a reagent for alcohol, 149
- Monazite sands, earths contained in, 202
- Monochloroglucosane, dichloralglucose in, 85
- Mononitroguaiacol, 302
- Monticello, Signor, and E. Scott, some geometrical instruments, 56
- Moreau, G., photography of metallic objects through opaque substances, 85
- Moreigne, H., determination of nitrogen in urine, 282
- Moreu, C., safron and isosafrol, 210
- Morin, 253
- Mourlot, A., properties of crystalline chromium sulphide, 35
- Muir, M. M. P., and L. Cohn, "Chemistry of Daily Life" (review), 303
- Muscular work, source and nature of the potential directly utilised in, 293
- Museums of Philadelphia, 96
- Murray, J. R. E., effect of X rays on the contact electricity of metals, 165
- Muthmann, W., and A. Clever, compounds of selenium with arsenic, 198
- Mylius, F., and O. Fromm, production of pure zinc, 24
- NAPHTHALENE derivatives, production of, 128
- tri-derivatives, 55
- Naphthylamine sulphonic acid, 54
- Nasini, R., and F. Anderlini, detection of argon, 233
- "Nebular Theory in Relation to Stellar, Solar, &c., Phenomena, Notes on" (review), 57
- Nessler's reaction, extension of, 134
- Newlands, J. A. R., the proper place of hydrogen, 305
- Newmon, K., and A. E. Salazar, "Comparative Cost in Chile of Gas and Electricity" (review), 221
- Newth, G. S., "Elementary Practical Chemistry" (review), 196
- "Newton and Argon" (review), 278
- Nicol, W. W. J., molecular volume of organic substances in solution, 54
- Nickel and cobalt boride, 141
- Nivengowski, G. H., observations on G. Le Bon's recent notes on dark light, 74
- Nitrates in potable waters, 269
- Nitric acid in the Seine, quantities of, 186
- detection, 251
- nitrogen, determination of, 2
- oxide, action of, 59
- reduction of, 95
- Nitrates, three new reagents for, 27
- Nitrogen, absorption of, 12
- atmospheric and chemical, combination with metals, 115
- combination of with magnesium, iron, copper, &c., 35
- determination of, 128
- fixation of, 47
- in urine, determination of, 282
- of the atmosphere to metals, direct combination of, 62
- and argon, separating atmospheric, 24
- peroxide, action of, 58
- Nitro-prussides, 142
- Nitroso-ruthenium compounds, 186
- Nitrosulphides of iron, 72
- Nodon, A., experiments with Röntgen rays, 85
- Nugues, E., and J. Chappuis, condition of the maximum of power of Crookes tubes, 202
- OEHMICHEN, R., law of noble metals during cupellation, 282
- Ohm, method of finding the true value of, 255
- Oil, Russian aniseed, 95, 164
- Oils and fats, bromine heat value of, 87
- Onnes, H. K., liquefaction of hydrogen, 219
- Optically active compounds, rotation of, 82
- Organic acid, constitution of a new, 194
- laboratories of the Technical High School of Dresden, researches, 23
- substances in solution, molecular volume, 54
- "Organic Compounds, Exercises in the Preparation of" (review), 22
- Orientation of living bacteria, influence of induction currents on, 233
- Osterberg, M., "Synopsis of Current Electrical Literature" (review), 256
- Oudin and Lannelongue, MM., application of Röntgen's rays in surgical diagnosis, 97
- and Barthelemy, MM., utility of photographs in human pathology taken with X rays, 61
- Oxidase, new, 293
- Oxidation experiments, 59
- of some gases with palladised copper oxide, 32, 52, 78
- Oxide, action of nitric, 59
- Oxides, rare, abundant source of some, 145
- Ozone, tubular generator for supersaturation with, 280
- PALMER, A. de F., wavelength of the D₃ helium line, 14
- Paraffin industry, 56
- Pararosaniline, synthesis of, 12
- Parmentier, P., solubility of sodium thiosulphate, 72
- Pasteur, industrial work of, 258
- Pavy, F. W., "Physiology of the Carbohydrates" (review), 34
- Pencils, litmus, 198
- Pentacarbon rings, synthesis of, 253
- Perchloric acid, preparation of, 8, 17
- Peridinitronaphthalene, 245
- Perkin, A. G., and H. Bablich, morin, 253
- luteolin, 105
- W. H., magnetic rotatory power of aromatic compounds, 301
- luteolin, 252
- jun., and W. H. Bentley, xylic and xylinic acid, 208
- and J. F. Thorpe, cis- and trans- methylisopropylsuccinic acids, 152
- and W. A. Bone, dimethylglutaric acids, 152
- symmetrical dimethylsuccinic acids, 152
- and E. Haworth, glycol, 105
- W. H. Bentley, phenoxyethylmalonic acid, 104
- Perrin, J., certain properties of Röntgen's rays, 61
- kathode rays, 61
- origin of Röntgen rays, 186
- Peteval, M., and Prof. Fleming, analytical study of the alternating current arc, 116
- Petroleum, flashing-point of, 186
- "Petroleum" (review), 130
- Phenoxyethylmalonic acid, derivatives of, 104
- Phenylhydrazin, reduction by means of, 186
- tartrate, 245
- Philosophy, Experimental, Batavian Society of, 4
- Philothion and iaccase, respective roles in seeds during germination, 48
- Phipson, T. L., abundant source of some rare oxides, 145
- presence of gold in silver ores, 71
- Röntgen rays in ordinary sunlight, 223
- Phosphate, rapid estimation of insoluble, 25, 47, 71, 94
- Phosphoric acid, determination of, 53
- acid, new, 48
- volumetric determination of, 212
- anhydride, molecular weight of, 103
- Phosphorescence, radiations emitted by, 141
- Photometric standard with acetylene, 59
- Photographic proofs obtained in darkness, 119
- Photographs in human pathology taken with X rays, utility of, 61, 186, 210
- in relief with Röntgen rays, 155
- Photography by Röntgen rays, 98, 189
- in colours, 213
- in the interior of the Crookes tube, 232
- of metallic objects through opaque substances, 85, 133, 144
- with dark light, 73, 74, 110, 121, 133, 269
- Phycomyces, action of X rays on, 210
- Physical Society, 56, 93, 116, 140, 162, 208, 243, 255, 290
- Physicians, meeting of the German naturalists and, 185
- Physiological study of Persian cyclamens, 291
- Picard, R. H., and F. Frankland, rotation of optically active compounds, 82
- Pictet, P., rapid determination of nitric nitrogen in vegetable products, 2
- Pig-iron, determination of graphite in, 31
- Piltchikoff, M. N., action of Röntgen rays on double and triple electrified strata, 223
- on X rays, 186
- Pinakones, production of, 153
- Pinene to citrene, relation, 127
- Plants, action of light and water in liberating the perfumes, 164
- action of various radiations of the solar spectrum on, 56
- identification of principal acids in, 295
- Platinum, fusibility of, 235
- Plumbic salts, 103
- Polarisation and diffraction of Röntgen rays, 201
- Pollard, W., and A. Hutchinson, lead tetracetate and plumbic salts, 103
- Polytechnic Institute, Northern, 287
- Ponzio, G., and M. Filetti, conversion of ketones into diketones, 107
- Pope, W. J., some substances which exhibit rotatory power in liquid and crystalline states, 267
- Poulenc, C., "Chemical Novelties" (review), 209
- Potash in soils, available, 83
- Potassium allo-camphorate, electrolysis of, 254
- &c., salts, optical relationships, 194
- fluorides and oxyfluorides, certain, 197
- permanganate and sulphuric acid, distillation, 122
- rubidium, and caesium, various investigations with, 195
- Potentials, depression of explosive by the X rays, 109
- "Pottery, Chemistry of" (review), 46
- Precious stones, action of X rays on, 186
- Preyer, W., argon and helium in the system of the elements, 235
- Prism, deviation of X rays by, 293
- Priwoznik, E., remarkable change in the structure of glass by heating, 48
- "Process Year-book" (review), 279
- Prost, E., composition of coal ash, 59
- Proude, J., and W. H. Wood, formation of so-called ammonium amalgam, 54
- Prud'homme, M., synthesis of pararosaniline, 12
- Pulfrich, C., and F. L. O. Wadsworth, spectral apparatus, 270
- Puling, M., kathode rays, 140
- Purdie, T., and S. Williamson, ethereal salts of optically active malic and lactic acids, 229
- Pyroigneous products, acidity of, 164
- QUINAZOLIN compounds synthesis of, 153
- RADIOGRAPHS, 257

- Ramsay, W., the Boyle lecture, 283
and J. N. Collie, argon and helium, 259
and M. Eumorfopoulos, determination of high temperatures by the melometer, 93
Ranver, F., application of photography by Röntgen rays to researches on vegetable matter, 211
Raum, W., and V. Meyer, prolonged action of low heating on detonating gas, 18
Rayleigh, Lord, argon and helium in the gas from Bath springs, 247
some physical properties of argon and helium, 75
Rays, new kind, 235
"Reagents, Repertory of Special" (review), 163
Redgrave, A. (the late), and H. S. Scrivener, "The Factory Acts" (review), 34
Redwood, B., and G. T. Holloway, "Petroleum" (review), 130
Reeves, J. H., addition to the Wheatstone's bridge, 140
exact value of Matthiessen's standard, 140
Reichenberg, S., gas analytical apparatus, 158
Resteen, A. D., "Molecules and the Molecular Theory of Matter" (review), 34
Resultant tones, 56
Revis, C., and F. S. Kipping, bromocamphor, 207
derivatives of hydrindone, 9
Rhamnose, rotatory property of superfluid, 48
Rhodinol, 166
extraction of, 153
Rice preserved over a century, 221
Richard, J., and T. Schloessing, jun., argon in the natatory bladder of fishes, 164
Richards on aluminium, report on his work, 306
Richards, T. W., and E. F. Rogers, revision of the atomic weight of zinc, 197, 226, 238, 250, 264
Rileal, S., and S. Rosenblum, analysis of chrome-iron ore, ferro-chromium, and chrome steel, 1
Righi, A., electrical phenomena produced by Röntgen rays, 109
reply to observations by, 257
Rings, pentacarbon, synthesis of, 253
"Rocks, Introduction to the Study of" (review), 22
Rogers, E. F., and T. W. Richards, revision of the atomic weight of zinc, 197, 226, 238, 250, 264
and Frith, Messrs., true resistance of the electric arc, 243
Röntgen, Prof., new discovery, 49
mechanical action emanating from the Crookes tube analogous to the photographic action discovered by, 98, 197, 211
rays, 163, 290
action of, 110, 223
deflection by magnets, 177, 189
diffraction, 212
diffraction and polarisation of, 201
diffusion of, 155
electrical phenomena produced by, 109
electrified, 198, 223, 245
facts relating to, 164
in ordinary sunlight, 223
novelty in photographs with, 144
origin of, 186
passage through liquids, 133
permeability to, 140
Röntgen rays, photographic researches on, 155
photographs in relief with, 155
resistance of some liquids and solids to, 177
silhouettes, 142
Röntgen's rays in surgical diagnosis, 97
certain properties of, 61, 110, 177, 280
method of application, 97
procedures, proofs obtained by, 62
Rose, E., and P. Jannasch, separation of metals in a current of carbonic acid charged with bromine, 24
Rosenblum, S., and S. Rideal, analysis of chrome-iron ore, ferro-chromium, and chrome steel, 1
Rossel, A., combination of atmospheric nitrogen with magnesium, aluminium, iron, copper, &c., 35
direct combination of the nitrogen of the atmosphere to metals, 62
Royal Society conversazione, 227, 289
M. Marey's official visit to, 11
Institution, 119, 142, 175, 199, 246, 284
Rubidium, cesium, and potassium, various investigations with, 195
Rübner, M., microscopic structure of clothing, 281
Ruhemann, S., and E. A., Tyler, ethylic aceto-acetate, 196
Ruoss, Prof., volumetric determination of metals, 247, 277
Russian anised oil, 95, 164
Rydberg, J. R., mechanical action emanating from Crookes tubes, 178
SABATIER, P., and J. B. Senderens, reduction of nitric oxide, 95
Safranines, certain novel, 35
Safrol and isosafrol, 210
Sagnac, G., diffraction and polarisation of Röntgen rays, 207
Sakurai, J., constitution of glycocine, 106
Salazar, A. E., and K. Newmon, "Comparative Cost in Chile of Gas and Electricity" (review), 221
Salts, absorption of moisture by deliquescent, 104
inversion of sugar by, 161, 173
mercurous, 83
of mercury, determination of, 198
of uranium, invisible radiations emitted by, 167, 189
optical relationship of potassium, rubidium, &c., 194
plumbic, 103
Samarium, new element in the rare earths contiguous to, 170
Sanitary Institute, 246
"Sanitation and Food" (review), 141
Sana, H. B., and A. Imbert, diffusion of Röntgen rays, 155
radiography, 257
stereoscopic photographs with X rays, 210
Sausages, colouration of, 281
Scheurer-Kestner, M., acidity of pyroligneous products, 164
Schloessing, T., amount of nitric acid in the Seine, 186
nitrates in potable water, 269
jun., composition of fire-damp, 119
and J. Richard, argon in the bladder of fishes, 164
Schmitz, K., and K. Cebo, production of pinakones, 153
Schnabel, C., "Manual of Metallurgy" (review), 22
Schneider, A., value of crude cresol, 169
Schranz, W., and P. Dobriner, determination of aniline, 236
of moisture in aniline, 270
Schutzenberger, P., and O. Boudouard, earths contained in monazite sands, 202
Schuyten, R. C., determination of mercuric salts, 198
Schwarz, F., new phosphoric acid, 48
Scott, E., and M. Monticolo, some geometrical instruments, 56
Scoville, W. S., and F. A. Gooch, reduction of selenic acid, 285
Scrivener, H. S., and the late A. Redgrave, "The Factory Acts" (review), 34
Sedgwick, W., "Argon and Newton" (review), 278
Seeds during germination, respective roles of phlothin and laccase in, 48
Séguy, G., a Crookes tube of a spherical form showing the reflection of the kathode rays by the glass and the metal, 72
tubular generator for super-saturation with ozone, 280
Selenic acid, reduction of, 273, 285
Selenium with arsenic, compounds of, 198
Senderens, J. B., and P. Sabatier, reduction of nitric oxide, 95
"Service Chemistry" (review), 10
Serpent's bites, immunity against, 142
Seubert, K., and K. Gaab, action of ferric chloride, 24
Shears, J. C., "Machinery and Appliances for Manufacturing Chemists" (review), 57
Shimer, P. W., determination of graphite in pig-iron, 31
Silicon, solubility of, 13
Silicide of copper, 119
Silver ores, presence of gold in, 71
"Single Salt Analysis" (review), 163
Smith, C., C. F. Cross, and E. J. Bevan, constitution of cereal celluloses, 228
Smoke, effect on agriculture, 225
Snape, H. L., action of diphenyldi-isocyanate upon amido-compounds, 57
certain thiocarbamates, 82
"Société d'Encouragement pour l'Industrie Nationale" (review), 279
Society, Batavian, of Experimental Philosophy, programme, 4
Chemical, 9, 40, 53, 68, 81, 91, 103, 126, 138, 150, 194, 206, 220, 228, 252, 266, 291, 301
Physical, 59, 93, 116, 140, 162, 268, 243, 255, 290
Royal, conversazione, 227, 289
M. Marey's official visit to, 11
Sodium alcoholate, action of, 81
in aluminium prepared by electrolysis, 64
sulphate, 252
thiosulphate, solubility of, 72
Soil, circulation of air in the, 72
Soils, available potash in, 83
Solar spectrum, action of various radiations on plants, 36
thermic maximum, spectral displacement of, 47
"Solar, Stellar, &c., Phenomena, Notes on Nebular Theory in Relation to" (review), 57
Sorel, E., distillation of the first acids of the fatty series, 245
Seu, composition of a white, 229
South African horse sickness, 246
Specific heat of hydrogen peroxide, 24
Spectral apparatus, 270
displacement of the solar thermic maximum, 47
Spectroscopic studies and chemical researches, 5, 15, 29, 39, 51, 66, 80, 88, 113, 124, 135, 147, 159, 171, 183, 192, 204, 216, 224, 241, 249, 263
"Spectrum Analysis" (review), 70
"Spiritual Heroes" (review), 21
Spivey, W. T. N., T. H. Easterfield, and T. B. Wood, charas, 207
Spring, W., specific heat of hydrogen peroxide, 24
Staats, G., yellow autumnal colouring matter of leaves, 85
Stanley, W. F., "Notes on the Nebular Theory in Relation to Stellar, Solar, Planetary, Cometary, and Geological Phenomena" (review), 57
Stas, J. S., chemical researches and spectroscopic studies, 5, 15, 29, 39, 51, 66, 80, 88, 113, 124, 135, 147, 159, 171, 183, 192, 204, 216, 224, 241, 249, 263
Steel and Iron, Institute, 198
casting of, 88
castings, Walrand - Legénisiel process, 111, 179
chrome, analysis, 1
for steel castings, 179
Steels, cemented open-hearth or Bessemer, 192
Stephens, F. R., and W. H. Symons, carbon dioxide, 252
Stereoscopic photographs obtained with X rays, 210
Storage cell of the future, 191
St. von Niementowski, synthesis of quinoxalin compounds, 153
Strange, E. H., E. Graham, and H. B. Dixon, explosion of cyanogen, 138
Straus, P., copper and manganese cyanides, 24
Streatfeild, F. W., and R. Meldola, mixed diazoamides, 129
relation between melting-point and constitution, 130
Subchloride of lithium, 35
Sugar, action on ammoniacal silver nitrate, 81
inversion by salts, 161, 173
Sulphate of barium, peculiar relations of solubility of, 276
Sulphide, cupric, existence of, 262
of chromium, properties of crystalline, 35
Sulpho-phosphides, new series, 156, 332
Sulphur, state of in the products of the combustion of coal-gas, 57
Sulphuric acid and lime, quantitative determination of, 285, 299
and potassium permanganate, distillation of aqueous solutions, 122
"Sulphuric Acid and Alkali, Manufacture of" (review), 268
Sunlight, Röntgen rays in ordinary, 223
Surgical diagnosis, Röntgen's rays in, 97
Swyngedauw, M. R., depression of explosive potentials, static and dynamic, by the X rays, 109
Symons, W. H., and F. R. Stephens, carbon dioxide, 252
TARDY, M., and G. Bouchardat, Russian anised oil, 95, 164
Tartrac acid, transformation of, 257
Teclu, M., our knowledge of flame, 197
Tellurium, 19
Temperatures, low, liquefaction of air and research at, 40
Terpene alcohols, extraction of, 232

- Textile goods, detection of Tus-
sah silk in, 236
- Thallium in relation to the gene-
sis of the elements, 304
- Thermic power of coal, calcula-
tion of, 91
- Thermodynamics, symbolism in,
203
- Thiocarbamates, 82
- Thiocinnamines, halogen addi-
tive products of substituted,
229
- Thiosulphate, solubility of so-
dium, 72
- Thomas, V., action of nitric oxide
on ferrous chloride, 59
action of nitrogen peroxide, 58
- Thompson, S. P., Röntgen rays,
290
- Thomsen, J., colour of the ions
as a function of the atomic
weights, 28, 198
re-calculation of the atomic
weights, 293
- Thorium oxide, abundant source
of, 145
and yttrium carbides, 164
- Thorpe, J. F., W. H. Bentley,
and W. H. Perkin, jun., cis-
and trans-methylisopropyl-
succinic acids, 152
T. E., "Manual of Inorganic
Chemistry" (review), 46
- Tilden, W. A., and R. E. Barnett,
molecular weight and for-
mula of phosphoric anhydride,
103
- Tin, lead, &c., analysis of alloys
of, 25
quantitative estimation of, 218
slag, analysis of, 88
sulphophosphide, crystalline,
119
- Tischendorf, P., action of chloro-
carbonic oxide, 17
- Titanic acid and iron in ores, de-
termination of, 123
- Titanium, crystalline, 47
- Tolidine and benzidine, valuation
of, 275
- Tommasi, D., new electrolyser,
280
- Tones, resultant, 56
- Toxic action of different alcohols,
293
- Toxicological detection of aqua
regia, 27
- Trades, Industries, and Arts Ex-
hibition, East London, 149
- Traeger, J., and P. W. Uhlmann,
oxidation experiments, 59
- Trillat, A., conversion of the so-
lution of liquid formaldehyd,
142
- Troost, M., hexagonal blende as
a substitute for Crookes
phials, 143
- Truffaut, G., and A. Hébert,
physical study of Persian cy-
clamens, 291
- Tsukanoto, M., toxic action of
different alcohols, 293
- Turnbull, W., and G. Duerr,
"Bleaching and Calico
Printing" (review), 58
- Turpin, G. S., "Practical Inor-
ganic Chemistry" (review),
34
- Tussah silk in textile goods, de-
tection of, 236
- Tutton, A., various investiga-
tions with potassium, ru-
bidium, and caesium, 195
volume and optical relation-
ships of the potassium, rubi-
dium, and caesium salts, 194
- Tyler, E. A., and S. Ruhemann,
ethyl aceto-acetate, 196
- UHLMANN, P. W., and J.
Traeger, oxidation experi-
ments, 59
- Umani, A., and A. Fontana, me-
chanical action emanating
from Crookes tubes, 211
- University of Freiburg, researches
from the laboratory, 23, 59,
107, 153
- Uranium carbide, 118
new radiations by metallic, 295
properties of, 296
salts, invisible radiations emit-
ted by, 167, 189
spark, temperature of, 142
- Urea, determination of, 103
- Ureas, &c., acidic, 230
- Uric acid, fermentation of, 257
- Urine, determination of nitrogen
in, 282
- VARET, R., mercurous salts,
83
- Vaubel, W., benzene nucleus, 59
solubility in water of certain
substitution derivatives of
benzene, 153
valuation of benzidine and to-
lidine, 275
- Vegetable alkaloids, acidimetric
estimation of, 287, 298
matter, researches on by means
of photography with Röntgen
rays, 211
- Venables, F. P., chlorides of zir-
conium, 25
- Vendt, G., quantitative deter-
mination of condensation
products, 23
- Vigorous, M., copper silicide,
119
- Violle, J., photometric standard
with acetylene, 59
- Volumetry, electrometric deter-
mination of the final point,
270
- Von Usler, C., separation of mer-
cury from arsenic and cop-
per, 28, 38
- WADSWORTH, F. L. O., and
C. Pulfrich, spectral appa-
ratus, 270
- Wales, H., and D. Carnegie,
volumetric composition of
ammonium chloride, 206
- Walker, J., and J. R. Appleyard,
transformation of alkylam-
monium cyanates, 82
and J. Henderson, electrolysis
of potassium allo-ethyl-
camphorate, 254
- Walther, R., constitution of di-
azobenzene compounds, 107
reduction by means of phenyl-
hydrazin, 186
- Wanklyn, J. A., and E. T. Chap-
man, "Water Analysis" (re-
view), 196
- Walrand-Légenisel process for
steel castings, 111, 179
- Warren, H. N., boron bronze,
262
deposition of aluminium from
aqueous solutions, 122
electro-dissolution and its uses,
37
new storage cell, 191
- Warrington, T. C., composition
of water 137, 145, 156, 170,
184
- "Water Analysis" (review), 196
- "Water, Potable" (review), 46
- "Water Supply" (review), 304
- Water, analysis of from the drop-
ping well at Knaresborough,
196
composition of, 137, 145, 156,
170, 184
constitution of, 26
evaporation, 281
examination of, 86
potable, 237
mounds of coal-ash and the
hardness of, 59
solubility in of certain substi-
tution derivatives of, 153
supply of London, 5, 65, 111,
146, 193, 241, 300
past, present, and future, 99
- Waters, potable, nitrates in, 269
- Wave-form, effect on the alter-
nate current arc, 209
- Wave-length of the D₂ helium
line, 14
- Wax, Chinese insect, 281
- Wells, H. L., and W. L. Mit-
chell, volumetric determina-
tion of titanic acid and iron
in ores, 123
- Werner, A., and A. Klein, so-
called amido-chromates, 48
- Wheats, hard and soft, compo-
sition of flours by grinding in
cylinders, 35
- Wheatstone's bridge, addition to,
140
- Whitehead, C., tellurium, 19
- Wiesbaden chemical laboratory,
131
- Wiggins, F., and sons, mica mer-
chants, new address, 7
- Wilde, H., place of helium in the
classification of elementary
substances, 35
thallium in relation to the
genesis of the elements, 304
- Williams, B. P., "Chemical Ex-
periments" (review), 280
- Williamson, S., and T. Purdie,
etheral salts of optically ac-
tive malic and lactic acids,
229
- Wilsmore, N. T. M., and J. N.
Collie, production of naph-
thalene derivatives, 128
- Wilson, E. B., "Cyanide Pro-
cesses" (review), 118
H. A., size of atoms, 63
- Wilson, J. A., bromine heat
value of oils and fats, 87
- Wood, T. B., available potash in
soils, 83
- W. T. N. Spivey, and T. H.
Easterfield, charas, 207
- W. H., and J. Proude, forma-
tion of so-called ammonium
amalgam, 54
- Work of Pasteur, industrial, 258
- Wuillomont, M., Röntgen rays
in the eye, 186
- Wynne, W. P., and H. Arm-
strong, naphthylaminesul-
phonic acid, 54
tri-derivatives of naphthalene,
55
- X RAYS on electrified bodies,
action of, 211, 232, 245
rays, 73, 74, 85, 94, 96, 186, 280
action on the diamond, 121
action on phycomyces, 210
centres of emission of, 164
deviation by a prism, 293
depression of explosive poten-
tials, static and dynamic, by,
109
effect on glass, 143
effect on the contact electricity
of metals, 165
emanate from the anode, 119
in the eye, 186
of Prof. Röntgen, 49, 73, 85,
97, 232
on photographic plates, action
of, 245
permeability of metals for, 85,
97, 140, 155
photography with, 99, 189, 211
refraction of, 293
use of phosphorescent sub-
stances for rendering visible,
150
utility of photographs in
human pathology taken
with, 61, 186, 210
- Xylic and xylidinic acids, 208
- YELLOW autumnal colouring
matter of leaves, 86
- Yttrium and thorium carbides,
164
&c., oxide, abundant source of,
145
- ZENGER, C. V., photography
with X rays, 99
Röntgen silhouettes, 142
- Zinc, atomic weight, re-deter-
mination of, 197
and copper alloys, 168
production of pure, 24
revision of the atomic weight,
226, 238, 250, 264
- Zirconium carbide, new, 175
chlorides of, 25
- "Zoology and Chemistry, Ele-
mentary Agricultural" (re-
view), 93

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AND
SULPHATE OF POTASH
AND
SULPHATE OF SODA
AND
SULPHATE OF AMMONIA
AND
SULPHATE OF STRONTIAN
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ACTION OF ACETYLENE UPON IRON, NICKEL, AND COBALT, REDUCED BY HYDROGEN.

By HENRI MOISSAN and CH. MOURET.

BERTHELOT has been the first to establish that the alkaline metals, if slightly heated along with acetylene, yield acetylides decomposable in the cold by water, with the reproduction of gaseous acetylene.

On repeating the same experiment in presence of iron, Berthelot obtained a rapid destruction of acetylene, with a formation of empyreumatic carbides with coke and hydrogen, without a production of iron acetylide.

The existence of nickel carbonyl has led us to resume the action of acetylene in the cold upon certain metals prepared in a state of great porosity.

Iron, nickel, and cobalt have been obtained on reduction by hydrogen at the lowest temperature possible. For the precaution to be taken in this preparation see the memoir in the *Annales de Chimie et de Physique*, by H. Moissan (1880).

A Kipp's apparatus containing pure calcium carbide, prepared in the electric furnace, enabled us to have a regular delivery of gaseous acetylene. This gas, after being washed with water and passed into a flask filled with anhydrous glycerin, was then dried over calcium chloride and potassa recently fused in a silver crucible.

A three-way cock enabled us to cause the acetylene gas to arrive abruptly upon the reduced metal. This latter was arranged in a tube which was filled with hydrogen or which could be exhausted.

Under these conditions, as soon as the acetylene gas was present in large excess, there was produced a very lively incandescence on contact with the metal at the ordinary temperature of the laboratory. Abundant fumes appeared in the tube, and condensed in the cold parts of the apparatus. If the speed of the gaseous current was slackened the incandescence ceased, but reappeared as soon as it was again accelerated.

If the reduction of the metal has not been effected carefully, and at the lowest temperature possible, the reaction may not be produced; but it is sufficient to heat any point of the tube with a spirit-lamp to see the phenomenon appear distinctly. The incandescence then gradually spreads over a length which may extend to 15 to 20 cm.

This incandescence does not last more than from two

to three minutes; at the moment when a plentiful deposit of carbon is formed in the tube the obstruction is complete, the gaseous current is arrested, and the luminous points disappear.

This experiment is especially brilliant with iron, but it is also produced very distinctly with nickel and cobalt reduced with hydrogen.

The black powder which is found accumulated in the tube after the experiment consists of a light carbon, in which the metal is diffused. It resembles the ferruginous carbon studied by Grunner (*Annales de Chimie et de Physique*, Series 4, vol. xxvi., p. 8, 1872) in the reduction of iron oxides by carbon monoxide. This coal evolves hydrogen, and leaves a black ferruginous residue. This carbonaceous residue is so much the richer in metal as it is nearer to the reduced iron employed in the experiment.

The very dense vapours produced at the moment of the reaction may be easily condensed by means of a small glass worm bedded in ice. The liquid thus obtained is rich in benzene, this latter substance being accompanied by all the carbides which can be produced in this reaction, the formation of which has been studied by M. Berthelot.

Lastly, we have studied the gases produced, and observed that, as long as incandescence does not take place, the acetylene is not modified. No products condensable at -23 are formed, and the properties of the gas are not at all altered.

As soon as the reaction at any point extends to ignition the gas collected is pure hydrogen, as appears from the following analyses:—

	Gas, c.c.	After the cuprous reagent.	Acetylene, per cent.
Nickel	 6.8	6.5	4.4
"	 6.8	6.5	4.4
Cobalt	 10.4	9.5	8.6
Iron	 6.9	6.8	1.4
"	 7.0	6.9	1.4

The gaseous residue, after treatment with copper subchloride, is pure hydrogen. Eudiometric combustions have yielded us many quantities of carbonic dioxide scarcely appreciable, derived from a small quantity of vapour of benzene.

It results from these experiments that acetylene reacts at ordinary temperatures upon reduced iron, nickel, and cobalt, producing a great disengagement of heat. A portion of the acetylene is transformed, conformably to

the pyrogenous reaction described by M. Berthelot, into benzene and its polymers, whilst the chief part of the gas is split up into its elements, carbon and hydrogen.

This reaction is due to a physical phenomenon. The reduced iron, nickel, and cobalt are extremely porous, and absorb acetylene energetically. This absorption liberates a quantity of heat, which occasions the polymerisation, and ultimately the decomposition of the acetylene. Hence all the energy reserved in the acetylene (an endothermic compound, as M. Berthelot has established) becomes available. The totality of these reactions produces incandescence, and the phenomenon continues, becoming more and more accentuated until the carbon derived from the decomposition of the acetylene accumulates in the tube in a quantity sufficient to stop the afflux of the gas.

If this interpretation is correct every porous substance, such, *e.g.*, as platinum, should yield an identical result. This, in fact, we have been able to establish.

Platinum black was prepared by reducing platinum chloride with sugar in presence of solution of sodium carbonate. After washing with hydrochloric acid, and then successively with water, alcohol, and ether, it was dried *in vacuo* over sulphuric acid.

This platinum black was arranged in a tube of Bohemian glass, in which a vacuum had been made with the mercury pump. As soon as the acetylene came in contact with the platinum black, the latter became incandescent, and the reaction was produced as already described,—deposit of carbon, formation of hydrogen and of pyrogenous carbides.

Platinum sponge and platinised asbestos act in the same manner. If the phenomenon does not appear at once, it may be induced by applying a slight heat.

These essentially porous substances behave, therefore, like iron, nickel, and cobalt.

Finally, on diluting acetylene with an inert gas, such as nitrogen, we may hinder the production of incandescence, but the absorption of the gas nevertheless takes place slowly, and by degrees the metal is carbided and retain a little hydrogen.

We have not been able, under these conditions, to isolate any solid or liquid compound containing metal.

In conclusion, we may say that pyrophoric iron, nickel, and cobalt, *i.e.*, reduced at the lowest possible temperature and placed in contact with an excess of acetylene in the cold, decompose this gas with incandescence, producing charcoal, hydrogen, and pyrogenous carbides. This decomposition must be ascribed to a physical phenomenon—the porosity of the metals. The same phenomenon is observed with platinum sponge.—*Comptes Rendus*, cxxii., p. 1240.

SEPARATION OF SILVER FROM GOLD BY VOLATILISATION.

By Dr. JOSEPH W. RICHARDS, of the Lehigh University.

IN making the quantitative blowpipe assay for gold and silver, it is usual to treat 100 m.grms. of ore at a single fusion, yielding buttons which are too small to be weighed accurately, but whose weight must be found by measuring carefully their horizontal diameters.

As determined by Plattner (and often verified in the writer's experience), silver buttons weigh 0.6346 of the weight of spheres of silver of the same diameter as measured, and gold buttons 0.7506 of the weight of gold spheres. The buttons obtained usually weigh 0.5 to 1.5 m.grms. and the separation of the silver from the gold in buttons so small is a matter of considerable difficulty. Plattner remarks that no satisfactory method of separation in the dry way is known, and recommends the parting by nitric acid. Working, however, with buttons smaller than pin-heads, it is extremely difficult to boil two or

three times with nitric acid, to wash until the silver salt is all removed, and then to gather and melt down the gold, without losing a considerable proportion of the gold in three or four directions.

Knowing that, on long heating, silver gives a coating of oxide on charcoal, and that gold does not, I made experiments to determine whether silver could be thus separated from gold, and have found the method practicable. On heating to a bright yellow heat (not to whiteness) upon charcoal an alloy of gold and silver, before a sharp-pointed oxidising flame, the silver volatilises easily and steadily until there is less than 5 per cent of silver remaining in the gold. I estimate this volatilisation to take place a little above the melting point of copper, say at 1100–1200° C. To remove the remainder of the silver, the heat is raised nearly to whiteness, or to about the melting-point of steel (1500° C.). When the silver is entirely eliminated, the gold, at this temperature, begins to volatilise also; in fact, a trace of gold will be carried off with the last of the silver, and if the ash of the charcoal be white it will show a faint crimson coating close to the assay. When this coating is heavy enough to be seen without the use of a lens, the silver has been completely volatilised, and the remaining button is pure gold. The amount of gold necessary to give this coating is too small to be determined by weighing or measuring.

Having explained the principle made use of, I will give the further details of conducting the operation. The charcoal should be dense, so as not to burn away too quickly. Too light a charcoal will not stand the five or ten minutes' application of the oxidising flame without burning through the piece. It should also leave a white ash under the oxidising flame, so as to furnish a background on which to see the crimson gold coating which determines the end of the operation. I have found the dense, hard charcoal made by Johnson and Co., of New York, to answer these requirements admirably. It is well, also, to work with a porcelain saucer, or large sheet of clean paper, under the flame, to catch the button in case it should be blown from the charcoal.

In order to perform this separation without excessive exertion, I would recommend that a gas flame not over 2 centimetres high be used, that the tip of the blowpipe be advanced at least halfway through the flame, and inclined somewhat sharply downwards, at an angle of about 45°. By observing these simple directions, a very sharp-pointed, needle-like oxidising flame will be produced, about 1 centimetre in length to the blue tip, which I have found the best for the purpose in view. To produce this the blowing need not be strong, but it should be kept up steadily. The button, in a shallow cavity near the end of the stick of charcoal, is now brought directly in front of the point of the flame, at about 1 to 2 millimetres from the visible blue tip. Its position, of course, is regulated by the temperature observed. The button should not, at this stage, be heated to whiteness, else the silver will boil and cause a loss by sputtering. The charcoal is held inclined towards the flame at an angle of about 30°, so that the flame descends almost vertically upon the button, and thus decreases the liability of its displacement by the force of the blast.

It will be found practicable to continue a blowing for about three minutes without discomfort, at the end of which time the operator may stop to observe the colour of the button. Supposing the alloy, on starting, to have been white, it will usually become pale yellow in from three to six minutes. When the alloy exhibits a brass-yellow colour, the heat should be raised, and the next blowing continued for not over two minutes. At the end of this time the alloy will usually exhibit nearly the pure gold colour, but no gold coating; or, at most, only a trace of it will be seen on the charcoal. After this, the heat should be raised to nearly whiteness, and then continued for not over one minute at a time. If a faint gold coating appears, further heating for one minute will usually develop a distinct crimson coating, visible without

the lens, and the alloy will show the pure gold colour. It is then taken out, cupelled, and measured.

If the amount of gold present be very small, it is difficult to continue volatilising silver after the button gets smaller than $\frac{1}{4}$ millimetre in diameter. The difficulty is caused by the ash of the charcoal, which, fusing to a slag, envelopes the button. To continue the removal of the silver, should the button arrive at this size without showing the gold colour, the operator cupels and measures a pure gold button of about the same size and adds it to the button being treated. The enlarged button is now worked down to pure gold, as before, removed, cupelled, and measured. The weight of gold obtained is diminished by the amount added, the difference giving that in the ore.

If the heating to incipient whiteness be continued two or three minutes after the visible gold coating is obtained, a very pretty gold coating of bright, peach-blossom colour is obtained, and a sensible amount of gold is lost by volatilisation. A pure gold button, 1 millimetre in diameter, weighing 7.58 m.grms., lost 0.03 m.grms. (0.4 per cent) each minute that it was heated to whiteness, and in five minutes gave a beautiful crimson coating. A silver button of similar size lost 18 per cent of its weight, each minute, at only a bright yellow heat. I estimate the point at which gold begins to volatilise as about the melting-point of soft steel (1500° C.). It is certainly considerably below the melting-point of platinum (1775° C.).

In conclusion, I wish to say that I have tested this method of separation in many different ways, with large and small buttons, and upon alloys rich and poor in gold, and have found the separation to be absolute when the conditions above described are properly observed. I have repeatedly alloyed a gold button with different amounts of silver, and then driven off the silver, the button, after two or three of such separations, remaining of exactly the same size and weight as at the start. In proposing this method of separation, I do not wish to disguise the fact that, to ensure success, it demands a steady hand and an experienced operator, and some practice; but I believe that any one who has mastered the art of blowpiping sufficiently to make gold and silver assays, can, in a short time, master this method of separating the gold and silver.

(In the discussion of the above paper, it was suggested that the method might be practicable in the ordinary assay of gold and silver, as, at assay offices, if an electrically heated furnace could be devised, in which the buttons could be placed on suitable supports, and kept at the proper temperature to volatilise silver, with a current of air passing over them. The movement to the hottest part of the furnace would suffice to remove the last traces of silver, just as the last traces of lead are removed in cupellation in an ordinary muffle. The process of removing the silver would then resemble cupellation in its general outlines, except that the temperature would be about 300° to 500° higher.)—*Journal of the Franklin Institute*, June, 1896.

THE IODOMETRIC DETERMINATION OF SELENIOUS AND SELENIC ACIDS.*

By F. A. GOOCH and A. W. PEIRCE.

It has been shown in a recent paper from this laboratory (Gooch and Reynolds, *Amer. Journ. of Science*, 1, 254) that the simple contact of solutions of selenious acid, potassium iodide, and hydrochloric acid, according to the recommendation of Muthman and Schäfer (*Ber. d. Chem. Gesell.*, xxvi., 1008) is not enough to effect the liberation of the theoretical amount of iodine when the assump-

tion is made that the selenium of the selenious acid is all reduced to the elementary condition. On the other hand, it was found that the yield of iodine is complete when such mixtures are submitted to distillation under well-defined conditions. It is necessary, however, to estimate not only the iodine which passes to the distillate, but that which is retained in small proportion in the residue, and, though this method of proceeding yields closely accurate analytical results, and is by no means difficult, it is obvious that a process so contrived that the reduction of the selenious acid should be registered entirely in the residue would possess the advantage in point of convenience. We have made the attempt, therefore, to apply in this case a principle of action laid down in a method elaborated in this laboratory for the estimation of chlorates (Gooch and Smith, *Amer. Journ. of Science*, xlii., 220). When a solution of arsenic acid containing potassium iodide and sulphuric acid is boiled under defined conditions (Gooch and Browning, *Amer. Journ. of Science*, xxxix., 188) the arsenic acid is reduced to arsenious acid with liberation of iodine. When the arsenic acid is in excess the whole of the iodine is evolved and the arsenious acid produced is its exact measure. Upon making the solution alkaline with acid potassium carbonate, the arsenious acid may be re-oxidised by standard iodine, and the amount of iodine thus used will be the exact equivalent of that set free in the reduction process. If, however, any other substance more easily reducible than arsenic acid is present, such substance should, naturally, take its part in liberating iodine from the iodide, and the reduction of the arsenic acid should be correspondingly less. This was found to be the case when a mixture containing a chlorate, arsenic acid, potassium iodide, and sulphuric acid was boiled under regulated conditions, so that, with a knowledge of the amount of iodide employed and the determination of the quantity of iodine necessary to re-oxidise the arsenious acid produced, the data were at hand for calculating the amount of chlorate present in the mixture. It was our hope (which proved to be well founded, as the sequel shows) that selenious acid would behave like a chlorate under similar conditions.

Pure selenium dioxide was prepared by oxidising presumably pure selenium in strong nitric acid, evaporating the solution to dryness, dissolving the residue in water, treating the solution with barium hydroxide until precipitation ceased, filtering, evaporating the filtrate to dryness, subliming the selenium dioxide from the residue, and re-subliming that product in a current of dry oxygen (which we found to be vastly more convenient and effective than dry air) until it was perfectly white and crystalline. From the oxide thus made a standard aqueous solution was prepared, from which portions were measured and (for the sake of greater accuracy) weighed for use in the experiments to be detailed. To each weighed portion of the selenious acid, contained in an Erlenmeyer flask of 300 c.m.³ capacity, was added a weighed amount of potassium iodide (somewhat in excess of that theoretically required) prepared in solution of convenient strength and tested as to its reducing power upon arsenic acid under the conditions of the experiments; a solution containing about 2 grms. of pure di-hydrogen potassium arseniate was introduced; and finally 20 c.m.³ of sulphuric acid of half-strength. Protected from ordinary mechanical loss by a trap (consisting of a two-bulbed drying tube, cut short and hung loosely, with the wide end downward in the mouth of the flask), and from violent ebullition by the introduction of a few bits of porcelain, the liquid was boiled until the volume decreased according to indicating marks on the flask from 100 c.m.³ or more to 35 c.m.³, concentration to about this lower limit having been found to be necessary to the completion of the reaction. The residue was cooled, the acid was nearly neutralised with potassium hydroxide, acid potassium carbonate was added until it was present to the amount of 20 c.m.³ of its saturated solution in excess of the

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. i., Jan., 1896.

quantity needed to complete neutralisation, and, after the addition of starch, standard iodine was introduced until the starch-blue appeared. The iodine introduced measured the arsenious acid (and so the quantity of iodine set free by the arsenic acid), and the difference between it and the iodine originally present in the form of the iodide represents the amount set free by the selenious acid.

The following table comprises the details and results of a series of determinations made in the manner outlined:—

Se = 79.1, O = 16.

Initial volume.	Final volume.	H ₂ SO ₄ half-strength.	Di-hydrogen-potassium arseniate.	KI taken.	SeO ₃ taken.	SeO ₃ found.	Error.
C.m. ³	C.m. ³	C.m. ³	Grm.	Grms.	Grm.	Grm.	Grm.
100	35	20	2	1.3277	0.1280	0.1275	0.0005—
"	"	"	"	1.0429	0.0998	0.0994	0.0004—
"	"	"	"	1.0887	0.1024	0.1028	0.0004+
"	"	"	"	1.0405	0.1036	0.1028	0.0008—
"	"	"	"	1.0721	0.1030	0.1029	0.0001—
"	"	"	"	0.9958	0.1273	0.1272	0.0001—
125	"	"	"	2.0828	0.1997	0.2000	0.0003+
"	"	"	"	2.2272	0.2110	0.2113	0.0003+
"	"	"	"	2.1535	0.2067	0.2069	0.0002+
150	40	"	"	2.6554	0.2560	0.2549	0.0011—
175	35	"	"	3.2428	0.3110	0.3118	0.0008+
"	35	"	"	3.2428	0.3085	0.3083	0.0002—

Obviously the reduction of selenious acid by this method is regular and accurate.

When similar treatment was applied to selenic acid, it became apparent that the arsenic acid attacked and destroyed the iodide before the selenic acid had been completely reduced. It is plain, therefore, that the selenic acid must be reduced to the condition of selenious acid before its estimation by the iodide method can be attempted. Ordinarily the simplest mode of reducing selenic acid is by boiling it in solution with hydrochloric acid of definite strength (Gooch and Evans, *Amer. Journ. Sci.*, 1, 400), but in this case the presence of hydrochloric acid is precluded on account of the consequent volatilisation of arsenious chloride during the process of concentration in the subsequent treatment with the iodide. It has been shown, however, in a recent paper from this laboratory (Gooch and Scoville, *Amer. Journ. Sci.*, 1, 402), that selenic acid is easily and completely reduced to selenious acid by potassium bromide and sulphuric acid under defined conditions. Moreover, arsenious bromide is not volatilised appreciably under the conditions. We made the attempt, therefore, to effect the iodometric determination of selenic acid by first reducing it to selenious acid by the bromide process, and then treating the residue with arsenic acid and potassium iodide in the manner described.

Selenic acid was prepared in standard solution by treating a known weight of pure re-sublimed selenium dioxide by a strong solution of potassium permanganate, in presence of a moderate amount of sulphuric acid, until the purple colour was distinctly visible, dissolving the precipitated oxide of manganese by oxalic acid, again adding permanganate until the final colour of faintly visible pink was permanent for a half-hour or more, and diluting to a fixed volume. Portions of the solution of selenic acid were measured into counterpoised Erlenmeyer flasks of 300 c.m.³ capacity and weighed, 1 gm. of potassium bromide was added, and sulphuric acid in such quantity that the total amount of the free acid should correspond to 20 c.m.³ of the acid of half-strength. The solution possessing a volume of 60 c.m.³ to 100 c.m.³ was boiled until the clear colourless solution left when the bromine vanished began to colour again. Experience

showed that the reappearance of the brownish colour is very easily seen, and that it is not safe to conclude that all free bromine has been eliminated, under the conditions of dilution and proportion, until this stage of concentration—which corresponds to a volume of about 35 c.m.³—has been reached; but the distillation should not be pushed beyond the point at which the returning colour is noted. When this condition was reached the solution was cooled, and treated exactly in the manner described for the reduction of selenious acid. The neutralisation by acid potassium carbonate, after the final boiling, generally occasioned the precipitation of manganous carbonate, but the precipitate did not interfere in the slightest with the titration which followed.

The following table comprises the determinations which were made to test the accuracy of the iodometric determination of selenic acid by the combined processes of reduction:—

SeO ₃ taken as H ₂ SeO ₄ .	KI used in second reduction.	SeO ₃ found.	Error.
Grm.	Grms.	Grm.	Grm.
0.0378	0.6306	0.0380	0.0002+
0.0378	0.5643	0.0374	0.0004—
0.0516	0.7136	0.0517	0.0001+
0.0503	0.7302	0.0508	0.0005+
0.0541	0.6671	0.0544	0.0003+
0.1007	1.3277	0.1011	0.0004+
0.1008	1.3277	0.1011	0.0003+
0.1007	1.2082	0.1005	0.0002—
0.1007	1.1684	0.1016	0.0009+
0.1007	1.0522	0.0999	0.0008—
0.1009	1.2679	0.1005	0.0004—
0.1031	1.1119	0.1032	0.0001+
0.1870	1.8720	0.1879	0.0009+
0.2014	1.9915	0.2020	0.0006+
0.2016	2.0745	0.2025	0.0009+
0.2059	1.8687	0.2064	0.0005+

It is plain, therefore, that selenic acid may be determined iodometrically with accuracy by first reducing it to the condition of selenious acid by treatment with potassium bromide in presence of sulphuric acid, in the manner described, and then completing the reduction to the elementary condition by the treatment with potassium iodide and potassium arseniate.

GROUND MINERAL PHOSPHATE AS A FERTILISER.*

By FRANK T. SHUTT, M.A., F.I.C., F.C.S.

THE finely-ground mineral phosphate (apatite), according to experiments made in our laboratory at Ottawa, is but very slightly soluble in 1 per cent citric acid solution. Thus, my results, obtained when using such a solvent in the proportion of one part of phosphate to 100 of the solution, showed that when treating a finely-ground phosphate containing approximately 25 per cent of carbonate of lime, only 6.2 per cent of the total phosphoric acid was rendered soluble. In other words, 1.5 per cent, approximately, of phosphoric acid had passed into solution by this treatment. Science has, therefore, corroborated practice, in showing that the ground mineral phosphate cannot be regarded as an economical source of available phosphoric acid, though undoubtedly the fineness and specific hardness of the material largely determines its exact value in this respect.

Chemical Experiments towards rendering available the Phosphoric Acid of Mineral Phosphate.

From these results it became apparent that a previous treatment of the mineral phosphate was desirable and,

* From the "Report on Experimental Farms to the Department of Agriculture, Canada."

indeed, necessary, if it was to be applied with a view to immediate returns.

To this end various experiments have been made in the laboratory of the Central Farm since 1893 towards a means of cheaply and effectively converting the phosphoric acid of ground phosphate into soluble and available forms, by means of the sulphates and bisulphate, and carbonates of the alkali metals. The first report on these experiments is contained in the Report of the Minister of Agriculture for 1893. It is there shown that the fusion of one part of finely-ground phosphate with the bisulphate of soda renders soluble a large proportion of phosphoric acid. Thus, in one instance, phosphoric acid equivalent to 38.49 per cent of apatite had been so converted. I may be allowed to quote from that report my conclusions as to the solubility of the phosphoric acid after ignition with the sulphates and bisulphates of soda and potash:—"I infer from these results (1) that any soluble phosphoric acid that may be formed during the ignition of the mineral phosphates with the sulphate of soda and potash, immediately re-combines in the presence of water to form tricalcic phosphate, and (2) that the ignition of the mineral phosphates with the bisulphates of soda and potash produces, according to circumstances, more or less soluble phosphoric acid.

"This latter conclusion is a very important one, since it is possible that by using the by-product, sodium bisulphate, an economical method for the treatment of mineral phosphates may be devised. It is scarcely necessary to add that such a process would prove of great value to Canada and Canadian agriculturists. Before an affirmative statement can be made regarding the commercial success of such a method for converting and utilising our phosphate, the cost of the raw materials and of the treatment, as well as the price obtainable for the manufactured article, must be taken into careful consideration."

Since 1893, further work had been done, the details of which have not yet been published. These latter experiments comprise the following:—(A) Heating together finely-ground phosphate and sulphate of soda, and treating the residue with 2 per cent of citric acid solution. The results showed that phosphoric acid equivalent to 35 per cent to 37 per cent of the phosphate had been dissolved.

(B) Ignition of the finely-ground phosphate with sodium bisulphate and treatment of the mass with 2 per cent citric acid solution. In this case 50 per cent of the apatite was found to have been rendered soluble in the acid solution.

The by-product that was used in these experiments contained only a small proportion of bisulphate, the larger part being sulphate of soda. It did not yield, therefore, as large an amount of soluble phosphoric acid as when pure bisulphate was used.

These experiments, the results of which I have condensed, were made before the appearance of Dr. Dyer's paper before referred to. Consequently, I was not then aware that 1 per cent citric acid represented the acidity in root sap. My solvent was undoubtedly too strong to give results which would allow us to say that the percentages of phosphate above stated are such as are rendered immediately available for plant use. Nevertheless, we may safely draw the conclusion that ignition of the finely-ground phosphate with sulphate of soda, as well as the by-product, bisulphate of soda, does convert a considerable amount of phosphate into a form much more readily available than the phosphoric acid in the untreated material.

I intend to repeat these experiments, using 1 per cent citric acid solution for the treatment of the ignited mass.

(C) The third series of experiments in this investigation conducted by us affords data regarding the effect of igniting finely-ground phosphate with (1) wood ashes and (2) carbonate of potash. A mixture of wood ashes and finely-ground phosphate was heated together, and the mass subsequently treated with water. In the aqueous

extract, phosphoric acid equivalent to 1.25 per cent of the phosphate was found. The residue, after treatment with water, was left over night in a 1 per cent solution of citric acid; this brought into solution phosphoric acid equivalent to 3 per cent of the phosphate. As the duplicate experiment in this trial closely agreed, we must infer that simple heating with wood ashes does not appreciably improve the solubility of the phosphoric acid in the mineral phosphate.

In the next experiment sand was added to the wood ashes and ground phosphate before ignition. This method was not found to increase the percentage of available phosphoric acid over that found in the preceding experiment.

Trials were then made by fusing together carbonate of potash and finely-ground phosphate. Treatment of the mass with water dissolved phosphoric acid equivalent to 6.5 per cent of the phosphate, and the subjection of the residue to the action in the cold of 1 per cent citric acid further dissolved phosphoric acid corresponding to 43.00 per cent of the phosphate.

From these experiments, I conclude that ignition with wood ashes does not materially increase the availability of the phosphoric acid in apatite, but that ignition with carbonate of potash does so very materially. If commercially any of the processes that comprise heating ground phosphate with the sulphates and bisulphates or carbonates of soda or potash are practicable, undoubtedly we have a means of readily rendering more or less immediately available much phosphoric acid now locked up and well-nigh useless to agriculture.

I may point out that if the potash salt were used in the fusion, the resulting fertiliser would contain, in addition to the available phosphoric acid, another element of almost equal importance to farm crops, viz., potash.

ON CEMENTATED STEELS.

By SERGIUS KERN, M.E., St. Petersburg.

IN the CHEMICAL NEWS, vol. lxxiii., p. 192, we gave a description of our process for crucible-steel melting, with a note upon cementated steels, which are necessary for the process. We prepared the steels for trials, in the steel foundry of the St. Petersburg, Naval Port (New Admiralty), as follows:—

As we had no special furnace for cementation, we made experiments, using plumbago crucibles 13 inches high and 10½ inches in diameter instead of cementation-boxes. The crucibles were heated in ordinary crucible coke furnaces usually employed for copper melting. Two experiments were made, and each time about 50 pounds of cementated steel was obtained.

1. *Charging the Crucible.*—On the bottom was placed a layer of charcoal 4 inches in thickness; next a layer of rounds, obtained from the punching of open-hearth steel ship-plates (0.18 per cent of carbon). On this layer 2 inches of charcoal were placed, next a layer of rounds, a layer of 2 inches of charcoal, a layer of rounds, and, finally, all the top was filled with charcoal. A burnt clay plug was fitted and well plastered with clay.

2. *Operation of Cementation.*—The crucibles were heated in the furnaces for four and a half hours, and during this time, at the middle of the operation, a fresh charge of coke was made. At the end of the operation, the lids of the furnaces were covered with clay all over the seams. The crucibles remaining in the furnace, to cool, for twenty-four hours. On opening the crucibles, all the three layers of punchings were found to be melted together, and an ingot was found at the bottom of the crucibles which could be easily broken, having an earthy-greyish fracture, with numerous spots of graphite.

Analyses of several pieces from this ingot made at the Obouchoff Steel and Cannon Works, St. Petersburg,

showed the metal to contain, on the average, 3.60 per cent of graphite and 0.56 per cent of carbon.

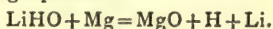
The cementated steel, mixed with soft wrought iron and other ingredients adopted in our process, was melted in crucible-steel furnaces, for the production of chisel-steel, the analysis of which is given in CHEMICAL NEWS, vol. lxxii., p. 192.

This process gives fair tool-steel for the works themselves, but certainly the process is not proposed for making high-class tool-steel for the trade. The cost of our steel in ready tools (forged at the Port) was about sixteen shillings per poond.

A QUICK NITROGEN ABSORBENT FOR THE LIBERATION OF ARGON AND MANUFACTURE OF METALLIC LITHIUM.

By H. N. WARREN, Research Analyst.

THE preparation of metallic lithium, which has up to the present been procured only in small quantities by the aid of electric currents upon the chloride, &c., has lately been simplified to a large extent. The author recommends for the preparation of that substance an iron tubulated retort, into which is introduced a suitable quantity of perfectly dry lithia, LiHO , and heated by means of a charcoal furnace; metallic magnesium in small pieces is from time to time brought into contact with the same through the tubular of the retort. A somewhat violent action takes place, and metallic lithium distils over according to the following equation:—



The carbonate may also be employed, but the metal is in the latter case accompanied by various quantities of lithium carbide, which, when thrown upon water, evolve acetylene gas.

As a nitrogen absorbent, either quick-lime or barium hydrate is saturated with a strong solution of lithia, ignited, and mixed with a sufficiency of magnesium powder, and the mixture allowed to reduce in an atmosphere of hydrogen gas at as low a temperature as possible. The resulting mass thus obtained contains metallic lithium in an extremely divided state, as also small quantities of barium or calcium, which has the power of absorbing nitrogen gas with the utmost facility, the mixture often becoming incandescent during the reaction.

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ON A REACTION OF CUPROUS COMPOUNDS WHICH MAY SERVE FOR THE RECOGNITION OF THE NITRITES.

By PAUL SABATIER.

IN contact with a solution of silver nitrate cuprous oxide totally displaces the silver, yielding a solution of cupric nitrate. After the solution of silver has been several times renewed there remains a grey matter, which Rose observed as far back as 1857 (*Poggendorf's Annalen*, vol. ci.), and which he considered as a mixture of metallic silver and an insoluble basic copper nitrate. On pursuing the study of this substance, which contains certainly not a cupric nitrate, but a cuprous nitrite, or a cuproso-cupric nitrite, I observed a special reaction, which I communicated, without explanation, at the meeting of the French Association for the Advancement of the Sciences, held at Bourdeaux, August, 1895. The grey matter, if carefully treated with an excess of concentrated sulphuric acid,

dissolves on it developing a magnificent violet blue colouration, which is immediately destructible by water, and which disappears spontaneously after the lapse of a few days.

A close examination of the reaction led me to conclude that the condition for its production is the simultaneous presence of concentrated sulphuric acid, of a nitrite, and a cuprous compound.

In order to obtain it the most conveniently, we dissolve suddenly a small quantity of dry crystalline sodium nitrite in concentrated sulphuric acid. If to the colourless limpid liquid thus obtained we add some quantities of red cuprous oxide, they immediately dissolve, yielding, along with a slight disengagement of nitric oxide, a very intense purple colour.

All the cuprous compounds, the bromide, iodide, chloride, hyposulphite, double cuproso-sodic, also all the cuproso-cupric compounds, such as the red sulphite and Schütte's violet blue ammoniacal hyposulphite, give the same reaction.

With dry cuprous chloride the action is not immediate, but it ensues after some time, with a certain escape of chlorine. The iodide yields a reaction which is not immediate, but very regular; nitric oxide is set at liberty, and all the iodine is eliminated in crystals, which may be removed by shaking the liquor with chloroform, which has no destructive action upon the purple matter.

Metallic copper obtained by reducing the pulverulent oxide with hydrogen acts strongly upon the nitroso-sulphuric liquid, and gives the violet colouration, with a very copious discharge of nitric oxide. Copper in sheets or turnings is only attacked after some time, and is surrounded with a violet sheath, which is gradually diffused in the liquid.

The cupric compounds give no reaction, nor is there any colouration with various metallic compounds of mercury, lead, silver, tin (stannous or stannic), manganese, cobalt, nickel, &c.

The same reaction may be produced with the solution of nitro-sulphuric acid, $\text{SO}_2(\text{NO}_3)\text{OH}$, in concentrated sulphuric acid, obtained in crystals by the action of sulphurous gas upon fuming nitric acid and suitably dried. But it is necessary to operate only upon solutions in a large excess of sulphuric acid.

Properties of the Purple Solution.—This solution, obtained with the cuprous compounds, is slowly decolourised, even if protected from air in a sealed tube. A rise of temperature favours the destruction, which is not immediate, even at 100° .

If shaken up in a flask with dry air it is promptly decolourised by oxidation, and a white precipitate of cupric sulphate is deposited. Oxidising agents, such as nitric acid, persulphuric acid, and lead peroxide, quickly produce the same result. Bromine decolourises it with production of black anhydrous cupric bromide.

Water, even if introduced with great care, so as to avoid a rise of temperature, destroys forthwith the violet compound. It is the same with sulphuric acid mixed with the fifth part of its volume of water.

Use of Nitrous Acid as a Reagent.—The reagent just described is a sensitive indicator of the nitrites. To detect the presence of a nitrite in a solution, we place he smallest possible drop on a white saucer, and upon it we place a drop of concentrated sulphuric acid, and we then let fall upon the liquid a few grains of cuprous oxide. If there is a nitrite, the violet tint appears at once.

The reaction, which is still very distinct with a solution containing per litre $\frac{1}{10}$ mol. of nitrous acid, is certainly less sensitive than that with metaphenylene-diamine.

The colouration is fugitive because the atmospheric moisture and oxygen contribute to its destruction. It is also interfered with by the presence of a notable quantity of nitrate.

In a future communication I shall show that the violet product obtained with the cuprous compound is simply the cupric salt of nitrosodisulphonic acid, a violet acid

which I have succeeded in preparing.—*Comptes Rendus*, cxxii., No. 24, p. 1417.

OZONIFEROUS ALDEHYDS FOR THE DETECTION OF MINIMUM TRACES OF IODINE IN PRESENCE OF CHLORINE AND BROMINE.

By E. LUDWIG.

It has long been known that ethereal oils can take up ozone, and retain it for a long time in a state capable of reaction. As it will be seen from the following, most aldehyds under certain circumstance possess this attribute, and can in consequence eliminate iodine. With this we may connect an observation made by Anato. Not the slightest iodine reaction was obtained with an ethanal, para-ethanal, propanal, methyl-propanal, or phenyl-methanal, if distilled in a current of carbonic acid, whilst a few drops of a distillation accompanied by a current of air suffice to show potassium iodide even in very dilute solutions.

For small quantities of iodine the sensitiveness of the reaction may be considered at least equal to the nitrite reaction. Even in solutions containing 1 part of iodine in 600,000 parts of water, the liberated iodine could be recognised as a permanent pale reddish colouration, if the smallest possible quantity of colourless carbon disulphide and a white background were employed.

I have tested the general applicability of the reaction, and found that it can be used successfully, although the solution must be neutral and contain no reducing agents, no mercurial salts, and no excess of the heavy metals.

It is a peculiar advantage of this reaction that even saturated solutions of bromides, free from iodine, do not react at all, whilst the presence of potassium iodide in a solution of 1/50,000 is sufficient, in spite of the bromides, to bring out plainly the reaction in carbon disulphide. The nitrite reaction fails already in solutions of 1/20 potassium bromide and 1/20,000 potassium iodide, so that the ozone-aldehyd reaction is about thirty times more sensitive.

A similar reaction is perhaps that recommended by E. Cook (*Chem. Society*, 1885, p. 471), in order to liberate iodine by hydrogen peroxide and acetic acid.

All aldehyds as yet examined, when pure, are alike capable of being used as reagents, and the only preparation needed is exposure to the air.

One c.c. of pure ethanal, poured into a 2-litre flask, could after an hour be used as reagent. After being kept for a day there was no considerable decrease of sensitiveness, but on the addition of water the reagent is decomposed in a very short time.

Para-ethanal, propanal, phenyl-methanal, can be at once obtained capable of reaction by distilling a small quantity, or the two latter by boiling up in a flask. In this state the normal aldehyds can retain their fitness for reaction, except methyl-propanal, which after a few hours requires to be again boiled.

Only the smallest possible quantities must be used. From 2 to 5 drops are sufficient for each reaction, and must be added carefully. The reaction succeeds best with phenyl-methanal, if we use 4 to 8 drops of an emulsion obtained by mixing 10 drops of aldehyd with 10 c.c. of water in a dropping-glass.

For recognising the iodine set free we may use starch-paste or carbon disulphide; the sensitiveness is considerably greater with the latter.—*Berichte*, xxix., No. 9, p. 1454.

Alimentary Value of a Bread obtained from Flour sifted to different Standards.—Aimé Girard.—A refutation of the assertion that bread made from fine flour is of an inferior alimentary value.—*Comptes Rendus*, No. 23.

RESEARCHES ON THE RÖNTGEN RAYS.*

By ALFRED M. MAYER.

1. The Röntgen Rays cannot be Polarised by passing through Herapathite.

HERAPATHITE is an iodo-sulphate of quinine, discovered by W. B. Herapath in 1852 (*Phil. Mag.*, March, 1852), and named herapathite by Haidinger. Herapath gives several formulæ for its production. The one which succeeded the best with me in giving crystal plates of large area is contained in *Phil. Mag.*, Nov., 1853. It is as follows:—

Bisulphate of quinine		3·24 grms.
Pyroligneous acid		56 c.c.
Alcohol (95 per cent)		56 c.c.
Solution of iodine (1 grm. in 11 c.c. alcohol)		50 drops.

The bisulphate of quinine is added to the mixture of pyroligneous acid and alcohol, and heated to 55° C., and then the iodine is added drop by drop while constantly stirring the solution. The vessel containing the solution is then placed on several layers of thick felt resting on a firm support to prevent vibration, and it thus remains about eighteen hours at a temperature of 8° C. At the expiration of that time large crystals will generally be seen floating on the surface of the liquid, the majority being at the bottom of the vessel. The solution gives, of herapathite, only 1-15th of the weight of bisulphate of quinine.

As suggested by Herapath, a microscope cover-glass is cemented to the end of a glass rod, with its plane at right angles to the rod, and is carefully brought under the floating crystal, very slowly brought up to it, and the crystal is thus secured on the surface of the glass. The mother-liquid is then absorbed from the glass by blotting-paper. If several crystals are desired on a cover-glass, a glass tube closed by the finger is brought over the crystals at the bottom of the vessel, the finger removed, then replaced and the tube taken out of the liquid. The crystals are allowed to sink into the drop at the end of the tube by holding the latter for some time in a vertical position: the drop is then brought in contact with a cover-glass. This is the manner in which I placed on the glass discs and blotting-paper the plates of herapathite used in my experiments.

Röntgen has shown that generally the lower the density and always the thinner the substance, the less it screens from a photographic plate the action of the X rays. Herapathite is, therefore, eminently fitted as the substance on which to make experiments which are to decide whether the X rays can or cannot be polarised by having traversed crystals which, like herapathite and tourmaline, transmit only one polarised beam, the other being absorbed by the crystal, for the density of herapathite is 1·557, and plates of only 0·012 m.m. thick are sufficient to answer the question. When crystals of herapathite 0·012 m.m. thick have their optic axes crossed at 90°, these crossed portions viewed against incident light appear black, so powerful is the polarising property of this substance. If the X rays be polarisable these black portions should act like thick lead, and completely screen the sensitive film from the action of the X rays. The fact is the crossed herapathites do not screen the X rays any more than the herapathites do when superposed plates have their axes parallel. In the latter case the crystals freely transmit light with a faint olive green tint.

The thickness of crystal plates used in the experiments varied from 0·01 m.m. to 0·025 m.m., as found by focussing with a micrometer-screw a powerful objective on the top surface of the crystals and on the glass on which they rested.

* From the *American Journal of Science*, vol. i., June, 1896.

Six discs of glass, 0.15 m.m. thick and 25 m.m. in diameter, were covered with herapathites in the manner described. They crossed one another at various angles; where they crossed at 90° the crossed portions were black. On a piece of yellow blotting-paper, $\frac{3}{4}$ m.m. thick, were also placed several layers of herapathites, so deep that they reflected a green metallic lustre like the elytra of cantharides. These discs and the blotting-paper were fastened to the slide covering the photographic plate. This slide was impervious to two hours' exposure to the actinic action of the sun's light. On the slide were also three discs of thin glass, so overlapping that the X rays had to pass through 1, 2, 3 thicknesses of the glass before reaching the sensitive plate. These served as standards with which to compare the screening effects of the herapathites.

The slide so prepared and covering a sensitive plate was exposed to the radiations of a Crookes tube in three experiments, for $\frac{1}{2}$, 1, and 2½ hours. On developing the plates, not the slightest trace of the presence of the herapathites was visible. The photographs of the glass discs had not the slightest mottling on their surfaces; appearing to the unaided eye and when examined through a magnifying glass with uniform illumination and grain throughout, and exactly like the photograph obtained by the X rays passing through a similar glass disc with nothing on its surface. The herapathites used in the experiments were so thin that they did not appreciably screen the X rays, whether the axes of the superposed crystals were parallel or crossed. But the action of the rays on the square of blotting-paper proved, even more conclusively, that the X rays cannot be polarised in this manner, for where this paper covered the photographic plate nothing was visible, except by careful scrutiny and with a favourable illumination, and then a mere ghost of the paper was detected, but with no traces whatever of the herapathites.

These experiments confirm in a convincing manner what Röntgen found by his experiments, viz., that the X rays cannot be polarised. At least, they cannot be polarised by passing through herapathite, which is by far the most powerful polarising substance known. It is unlikely that polarisation will be detected by using any doubly refracting substance which transmits two beams polarised in planes at right angles to each other; for if polarisation exist, the thickness of the substance required to get a measurable departure of the two rays so screens the X rays that a very small fraction of them (at least by calcite) will be transmitted; also, Röntgen is of the opinion that if the X rays be refrangible, the index of refraction is nearly unity even in such a highly refracting substance as ebonite, which has an index of about 1.6 ("On the Physical Properties of Vulcanite," by A. Mayer, *Amer. Journ. Sci.*, Jan., 1891). It is therefore reasonable to suppose that the difference in the refraction of the ordinary and extraordinary beams will be too small to be measurable in the faint shadowgraphs obtained by doubly refracting substances.

It remains to be decided whether the X rays can or cannot be polarised by reflection, Professor Rood having recently proved conclusively that they are reflected from platinum.

2. The Density of Herapathite.

Herapath gives 1.89, at 60° F., as the density of the very remarkable substance he discovered (*Phil. Mag.*, 1855, p. 369). As its density is interesting to have in connection with the experiments described above, I made two determinations of it by weighing about 0.3 gr. of the substance in water, and also by the displacement it gave of the water in a specific gravity flask. The mean of these two measures was 1.6. As this number differs greatly from that of Herapath, I thought that the small mass I had used was the cause of the discrepancy. I then made about 2 grms. of herapathite, freed it of its mother-liquid by washing with water at 0°, and dried it

at 25° *in vacuo*. When it had ceased to lose weight I weighed it in a specific gravity flask holding about 10 c.c., then just covered it with water, placed it *in vacuo* and agitated it, so that it would be freed of any air that might be contained in its mass. The flask was then nearly filled with water and again placed *in vacuo*, then entirely filled and weighed. I found from this carefully made experiment that the density of herapathite is 1.557 at 20° C.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, June 26th, 1896.

Captain W. DE W. ABNEY, President, in the Chair.

MR. F. BEDELL read a paper "On Admittance and Impedence."

The author discusses the application of the method of "vector diagrams" to the solution of questions connected with alternating currents. He shows how, by a consideration of the *loci* of the different lines on such a diagram, many problems which require for an analytical solution a lengthy investigation, may be simply and expeditiously solved.

MR. BLAKESLEY asked the author what was his test of resonance? Was it that the primary current and E.M.F. were exactly in the same or in opposite phase. The term resonance was an acoustical one, and he did not see why it should be applied to one particular case in the electrical problem.

MR. INWARDS asked what degree of accuracy the author had obtained?

The author, in reply, said that if the applied E.M.F. and the current were brought into phase by means of a condenser in the secondary, then he called that a case of resonance. The agreement between the experimental and theoretical results was generally within from 1 to 3 per cent.

Prof. S. P. THOMPSON read a paper "On the Properties of a Body having a Negative Resistance."

The author, after showing the consequences which would follow, according to the laws of Joule and Ohm, if we postulated the existence of a body having a negative resistance, goes on to show how the observations described by Messrs. Frith and Rodgers in a paper read at a recent meeting of the Society, only prove that that part of the resistance of an arc which is not constant is a positive resistance that varies inversely as the current. Since it varies inversely as the current, the term—

$$\frac{dR}{dC}$$

will be negative, and so will the quantity—

$$C \frac{dC}{dR},$$

which is what they have tabulated as a negative resistance. That the resistance of the arc itself should vary inversely as the current is natural, for it may be regarded as a column of vapour, the cross section of which is proportional to the current, and therefore increasing in its conductances in direct proportion to the current. There is no need even to suppose any (distributive) adjuvant E.M.F., which would be the other alternative to the suggestion they have made.

MR. SWINBURNE asked if the numbers on which Messrs. Frith and Rodgers based their arguments were obtained by taking successive readings of a voltmeter.

Prof. AYRTON said that what they maintained was, that it the arc acts as if it had a back E.M.F. and a

resistance, then the resistance is a negative quantity. In ordinary cases we do not know what really constitutes a resistance, but simply say that a circuit, in which electrical energy is being dissipated at a rate proportional to the square of the current, has resistance. If the loss is proportional to the first power of the current, then we say there exists a back E.M.F. Is it impossible to imagine a circuit in which a loss of electrical energy occurs proportional to the current and a return of energy to the circuit proportional to C? If in a curve showing the relation between V and C you draw a tangent at any point, it is not the tangent of the inclination of this tangent which Messrs. Frith and Rodgers have called the resistance; it is another quantity which they call the electrical—

$$\frac{dV}{dC}.$$

In conclusion, the author seems to have based his paper on three misconceptions:—(1) That it had been claimed that a negative resistance could exist alone; (2) that the curves given by Messrs. Frith and Rodgers showed that the ordinates were inversely proportional to the current; (3) that what was measured was the geometrical—

$$\frac{dV}{dC}.$$

Mr. FRITH said that in a paper by Mr. Rodgers and himself they had defined the resistance of the arc as the ratio—

$$\frac{dV}{dA}, \text{ where, by } \frac{dV}{dA},$$

they meant not what was ordinarily understood by this expression, but the value of the ratio obtained by superposing an alternating current on a direct current arc. In order to show that, in cases analogous with that of the arc, but in which the true resistance can be verified, the electrical—

$$\frac{dV}{dC}$$

obtained by superimposing an alternating current gives correct results for the resistance, some experiments have been carried out. In one case a glow-lamp was placed in series with some fifty ampère secondary cells, and a current sent through against the E.M.F. of the cells. The value obtained for the electrical—

$$\frac{dV}{dC}$$

agrees very well with the value of the resistance obtained by dividing the P.D. between the terminals of the lamp by the current. At very low frequencies for the superimposed alternating current, it is evident that the electrical oscillations could travel along the steady valve curve; and this is clearly the meaning of the critical frequency observed with cored carbons, namely, that under the critical frequency the superimposed alternating current travels on the steady valve curve, and over that frequency along the line joining the point on the curve and the instantaneous origin.

Mr. FRITH exhibited a mechanical model of the arc which he has devised. This model consists of two rods of carbon dipping in two mercury cups which are traversed by the current. The current also passes through a solenoid which attracts an iron core attached to the carbon rods, and draws them down into the mercury, thus reducing the resistance of the instrument. Hence it can be so arranged that the P.D. between the terminals decreases as the current increases. With this model it is found that, for superimposed oscillatory currents of such a frequency that the moving parts are not able to follow the changes in the current, the oscillations of the current and of P.D. are in phase, and the electrical—

$$\frac{dV}{dC}$$

gives the resistance of the apparatus for various currents.

Mr. CARTER asked the author how, in his vapour column theory, he explained the difference in the behaviour of solid and cored carbons.

Mr. ENRIGHT asked why it was absurd to suppose that a negative resistance could exist? Prof. Ayrton and Mr. Frith had made in their definitions certain restrictions: it ought, however, not to be necessary to make such restrictions.

Mr. BLAKESLEY asked if, since the title of the paper by Messrs. Frith and Rodgers was entitled the "True Resistance of the Arc," it was to be inferred, as the results given were negative, that a negative ohmic resistance existed in the arc. Mr. Thompson's paper appeared to him (Mr. Blakesley) to be rather a mathematical than a physical paper.

Prof. RÜCKER said that the discussion showed that considerable confusion existed, and that the introduction of the term negative resistance only tended to fog matters. It was entirely wrong to argue that because you have a quantity with a positive value, therefore a negative value must also be possible. As an example, take the case of mass. If you defined as a positive mass that which is attracted to the earth, and then found that cork when immersed in water was repelled from the earth, would you, therefore, say that cork had a negative mass? Is not "negative resistance" a term for which some equivalent could be found which would not lead to confusion?

Mr. HOVENDON made some remarks on his experiments.

The author, in his reply, said that he did not dispute the accuracy of the results obtained by Messrs. Frith and Rodgers, but it was the interpretation that they had given of their results to which he objected. Mr. Frith now makes a new reservation, namely, that the results depend on the particular way in which the increment of C and the decrement of V are made. He supposes that, if the experiment is made in a particular way, a new slope is obtained which is proportional to what we call the true resistance, and hence gets a new definition of the quantity—

$$\frac{dV}{dC}.$$

He (the speaker) endorsed all Prof. Ayrton had said as to the interest of the model exhibited. The question is, Is there anything in the arc which acts as a source of energy to the circuit either as a negative resistance or as an adjuvant E.M.F.? Mr. Frith's experiments do not give us any hint as to the point where the negative resistance occurs, and the absence of any such energy-giving portion of the arc, rendered probable by the fact that the arc itself is hotter than the crater. In reply to Mr. Carter, the anomalies which occur with cored carbons are so great as to prevent any argument being based on their behaviour.

The Chairman (Captain ABNEY) said that the mere fact that the quantity—

$$\frac{dV}{dC}$$

had been defined in two distinct ways showed that the definitions would have to be modified in some way.

Process for Dissolving Ignited Iron Oxide and other Metallic Oxides.—Hugo Borntrager. — The methods used for re-dissolving ignited ferric oxide are, for the most part, circumstantial and tedious. The author generates hydrogen from hydrochloric acid and flower-wire (i.e., the thin iron wire used by florists in making up bouquets, &c.), and adds the oxide in question. The oxide dissolves instantly, as the nascent hydrogen reduces it at once to ferrous oxide. The same holds good for many metallic oxides. The author is not in a position to say whether this procedure is available for determining the sulphur in burnt ores.—*Zeit. Anal. Chemie.*

NOTICES OF BOOKS.

Preserved Foods. ("Les Conserves Alimentaires.")
By J. DE BREVANS, Chief Chemist at the Municipal
Laboratory of Paris. Paris: J. B. Baillière et Fils.
1895. 18mo., pp. 396.

Now the chief seats of dense population are precisely those where the production of food is interfered with by want of space or by ungenial climates and barren soils, its preservation and transmission to the consumer must decidedly rank with the more useful arts. Hence we hold M. de Brevans as entitled to public gratitude for the compilation of the work before us. The preservation of foods involves questions of no little nicety. Decomposition must be obviated; the escape of volatile constituents must be prevented, if thereby the flavour and appetising character of the meats would be imperilled, and digestibility and assimilability must not be sacrificed. It is quite natural that a work of this character should be undertaken in France, where, sooner than in many countries, cookery has been recognised as an important department of chemistry.

The subjects principally here considered are the preservation of aliments of animal origin (butchers' meat, fish, milk, butter, and eggs), that of aliments of vegetable origin (vegetables and fruits), the decomposition of preserved foods,—our French neighbours use a more general term, "alteration,"—and the analysis of such preserved foods.

The methods of preservation may be classed in four groups:—

1. Procedures by desiccation and concentration.
2. Procedures by cold.
3. Procedures by sterilisation, with or without elimination of atmospheric air.
4. Procedures by antiseptics.

Most of the preserved foods met with in commerce have been produced by the joint action of two or more of these methods, and none of them have come into universal use. Liebig's extract of meat is, perhaps, most widely known and used; but the author remarks that the true rôle of extracts of meat is to serve as condiments, to enrich soup, gravy, &c., and they hence have but a slight importance in domestic economy. An extract of mutton produced in Australia has not given satisfaction.

The view of certain hygienists that extracts of meat are positively injurious, is a view which is combatted by Dr. Kemmerich.

Not a few extracts abundantly advertised in Britain are not mentioned here, whence we may suppose that they are little known on the Continent.

It is here laid down that a good extract of meat should contain no albumen, and at most 1·5 per cent of fat. It should not contain more than 21 per cent of water, and from 56 to 65 per cent of matter soluble in alcohol at 80°. Its proportion of ash varies between 15 and 25 per cent, principally sodium chloride and phosphates.

Papaine is inactive in an acid solution, but in an alkaline solution it digests in a few hours from 70 to 85 times its weight of meat. Gelatin-peptone, we are reminded, has scarcely any nutrient value. Some years ago *Les Mondes* informed us that an artificial peptone was being manufactured in Paris from a most revolting substance.

A biscuit used, at least experimentally, in the German army in 1885, is composed of wheat flour, lard, and beef, grated with a suitable quantity of salt and spices.

Sausages, which may be considered as a form of semi-preserved meat, seem to have been overlooked by the author. This is the more to be regretted since they often contain matter grossly unfit for human food and are in a dangerous state of decomposition, and require a bacteriological examination. The *hack-fleisch* of the Germans, which is simply raw sausage-meat without a skin, is one

of the forms in which trichinæ are introduced into the human system.

The use of borax for the preservation of alimentary matters is, at least, very questionable, and pending further inquiry it should be avoided. Its addition to wines, like that of salicylic acid, is denounced by the Consultative Committee of Hygiene in France.

We can strongly recommend this volume to hygienists and medical practitioners.

Alkali, &c., Works Regulation Acts, 1881 and 1892.

Thirty-second Annual Report on Alkali, &c., Works. By the CHIEF INSPECTOR. Proceedings during the Year 1895; presented to the Local Government Board and to the Secretary for Scotland. Ordered by the House of Commons to be printed, May 12th, 1896. Her Majesty's Stationery Office.

MR. A. E. FLETCHER, after ably filling the office of Chief Inspector for eleven years, has retired, and has been succeeded by Dr. R. Forbes Carpenter. Dr. A. C. Fryer has been advanced to the rank of full Inspector, in especial charge of the South Wales and South-west England districts. We have every confidence that the present staff will continue to work on the lines laid down by their predecessors.

The number of works now registered in Britain is 1191, of which 1065 are scheduled as alkali works. Since 1894 there has been a decrease of one alkali work and an increase of ten other works which come under the Acts.

As regards alkali works, frequently so-called, the escape of hydrochloric acid liberated is slightly over one-third of the legal standard. In like manner, the average amount of escape of acid compounds of sulphur and nitrogen is only 1·158 grain, and less than one-third of the legal standard, i.e., 4 grains calculated as sulphuric anhydride per cubic foot. The number of prosecutions has been only 9, all for non-registration.

The total salt decomposed in the alkali process has been 836,787 tons, a considerable increase. The ammonia-soda process now, however, takes the lead as to the quantity of salt decomposed, having consumed 428,614 tons as against 408,173 tons used in the Leblanc method.

Three electrical processes are now coming into operation, viz., the patents of Messrs. Holland and Richardson, carried out by the St. Helens Electro-chemical Co.; those of Castner and Kellner, being brought into operation at Weston Point, near Runcorn, by the Castner-Kellner Alkali Co.; and the Hargreaves and Bird's electrolytic process, which has been experimentally worked at Farnworth, near Widnes.

Full credit is here given to the United Alkali Co. for their care in keeping their plant in the highest state of efficiency and in preventing all leakage.

As regards the recovery of sulphur from tank-water by the Chance-Claus process, no notable improvement is recorded.

Our old friend the Sankey Brook still emits hydrogen sulphide into the air of St. Helens, and this renders it difficult to trace the source of any escape of this gas.

The Oldbury Alkali Co. are still producing cement from the slurry as it leaves the carbonators, and are confident that they can meet the demands of engineers.

Complaints of the escape of chlorine are now extremely rare.

The production of superphosphate in this country is now close upon a million tons, the amount in the United States being at least equal, that in Germany 600,000, in France 750,000, Belgium 300,000, Denmark and Holland 200,000, Italy 50,000. The total expenditure on agricultural chemicals is now above £22,000,000.

The production of ammoniacal salts in the United Kingdom, calculated as sulphate of ammonia, shows a considerable increase, and means an increase in the national wealth of more than 1½ millions yearly, obtained

mainly from sources formerly neglected. Among the secondary products of coke, benzol is being recovered to a serious extent.

It must not be forgotten that the production and sale of chemical works have to suffer heavily from the prolonged depression in agriculture,—a calamity for which relief is scarcely conceivable unless our electricians can do away with spring frosts and heavy rains in July and August.

The makers of cement have to contend with low wages paid by their Continental competitors.

Some relief seems obtainable by the disuse of open kilns. A case is quoted where a firm owns two works, one consisting of forty open kilns, whilst the other work is equipped with modern chamber kilns, slurry and clinker grinding-mills, &c. The whole of the work done by this firm during the year has been effected at the modern works, and the forty open kilns have stood idle.

It need scarcely be said that the export trade in cement is practically at an end.

The two great obstacles to the development of British chemical manufactures are the demand for a prohibitive scale of wages, especially in the coal trade, and the examinal system of education, of which not even the recent collapse of China has cured us.

The Parallelogram of Forces as Foundation of the Periodic System in Chemistry. ("Das Parallelogramm der Kräfte als Grundlage des Periodisches Systems in der Chemie.") By Dr. JOACHIM SPERBER. Zurich: E. Speidel. 1896.

THE author recognises the primary unity of all the elements which is demanded by the phenomena of allotropy.

Two points have struck him concerning the periodic system. In the first place, it is from the present point of view quite inconceivable that different quantities of one and the same primitive matter are equivalent; e.g., 1 part by weight of hydrogen, 7 parts of lithium, 22.99 sodium, 39.03 parts of potassium, 85.2 parts of rubidium are equivalent, and an equal quantity of matter is heterovalent; e.g., 35.37 parts by weight of chlorine can be from monovalent to septavalent. This the author holds—and here comes the nucleus of his hypothesis—is only possible if the atoms enter in combination at definite angles, so that the valence indicates only the value of the components which the atom supplies to the resulting compound.

Secondly, it is remarkable, and cannot be accidental, that the physical and chemical properties of the elements are periodical functions of the atomic weights, just as goniometric functions—sine, cosine, tangent, and cotangent—are periodical functions of the angles. In the periodic angular system the minimum of the angle of the equivalents is 70.47 for carbon; the maximum for the monovalent metals, gold, mercury, and thallium, is 89.70; greater angles, from 90° to 270°, would show a negative valence.

An element of the angular equivalence 0 would have no valence. Its atoms, therefore, would enter into no chemical combination and would oscillate at right angles to the longitudinal vibrations of the mols. of the other elements. This element might possibly be the cosmic ether. Recent researches, we may here add, point to the possible existence of such elements.

We find the remark that, from the point of view of the periodic angular system, the theory of a constant valence of the elements seems completely erroneous. The valence of an element depends on the angle at which it enters into combination. This angle can be modified by external agencies, pressure, temperature, electricity, light, &c.

The remainder of this pamphlet can be fully and fairly judged only by eminent mathematicians. We cannot help regretting that Dr. Sperber has not seen his way to

a statement of his theories in plain language, reserving mathematical developments for some future occasion. We find him (p. 26) referring to Boltzmann as having "in a mathematical way, in which a chemist can scarcely follow without dizziness," calculated the dissociation heat of iodine as 14.265 cal., whilst our author makes it as much as 21.0 cal. Respecting the hope that Dr. Sperber will be able to expound his theory in a form intelligible to chemists, we are of opinion that he has come upon truth which merely wants to be disentangled.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 23, June 8, 1896.

Study of Cast Vanadium and of Vanadium Carbide.—Henri Moissan.—This memoir will be inserted in full.

On a New Method of Preparing Alloys.—Henri Moissan.—The method of preparation indicated in the author's former paper for the alloy of aluminium-vanadium, by setting out from vanadium, is applicable to a number of oxides, and is founded on the powerful affinity of aluminium for oxygen. By this method I have been able to obtain alloys of aluminium with the majority of refractory metals which I had isolated by reduction in the electric furnace. The process consists in throwing into a bath of liquid aluminium a mixture of the oxide to be reduced and of aluminium filings. The preparation is effected in the dry way, and without the addition of any flux. I have thus obtained alloys of aluminium with nickel, molybdenum, tungsten, uranium, and titanium. We consider that this method is general, and will permit us to obtain a number of new alloys.

Nature of the Chemical Process which Governs the Transformation of the Potential from which the Muscles derive the Energy necessary for Work.—A. Chauveau.—The author's researches have been made from a perfectly general point of view. They form part of a total from which they have been withdrawn for the demonstration of the law of equivalence in the transformation of force in animals after a comparison of the positive and the negative work of the muscles.

Spectra of the Non-Metals in Melted Salts.—A. de Gramont.—This paper will be inserted in full.

Contribution to the Study of Capillary Affinities.—M. Lachaud.—The author examines some of the properties of animal charcoal, such as its hygrometric character, its action upon solutions, its behaviour with a mixture, the rôle of its porosity, the influence of molecular weight in a series, and a comparison of various blacks among themselves.

Determination of Potassa.—Charles Fabre.—This paper will be inserted in full.

Evaporation Heat of Formic Acid.—Miss Dorothy Marshall.—This research has been executed in Prof. Ramsay's laboratory at University College.

Combination of Antipyrine with the Oxybenzoic Acids and their Derivatives.—G. Patein and E. Dufan.—The authors examine the action of antipyrine with sodium salicylate, with methyl salicylate, with anisic acid, and with saligénine.

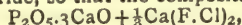
Composition of the Red Pigment of Amanita muscaria.—Dr. A. B. Griffiths.—This pigment has the composition $C_{19}H_{18}O_6$. It is insoluble in water, but

soluble in chloroform and ether. Its solutions do not give in the spectroscopic characteristic absorption bands.

On Lighting with Acetylene. — G. Trouvé. — This paper requires the three accompanying figures.

No. 24, June 15, 1896.

The Variations observed in the Composition of Apatites. — Adolphe Carnot. — The crystalline calcium phosphates contain a uniform proportion of calcium fluoride or chloride, so that the composition is—



or, in the unitary notation, $\text{Ca}_5\text{P}_3\text{O}_{12}(\text{F}, \text{Cl})$. It is remarkable that the only instance known of a tribasic calcium phosphate free from the normal proportion of calcium fluoride, chloride, and even carbonate, is deprived of any external crystalline form, although it presents the cleavage and the optical properties of a true apatite.

Alimentary Value of Bread made from Flours sifted to different Degrees. — Aimé Girard. — Really useful bread, which man ought to prefer if careful of his health or of his pocket, is made from flour sifted to the degree of 60, 65, and even 70 per cent. The rule for a truly economical use of the grain of wheat is to reserve at most 70 per cent for human consumption in the form of bread, and at least 30 per cent for feeding cattle. What man does not take in the form of bread, he recovers in the state of meat.

Dissociation-Spectra of Melted Salts. Alkaline Metals: Sodium, Potassium, Lithium. — A. de Grammont. — In studying the line-spectra of the non-metals in salts melted by means of the spark strongly concentrated, it is advantageous to make use of the salts of the alkaline metals, on account of the simplicity of their spectra. We need merely deduct from the entire spectrum a small number of known rays to have those of the non-metal in question. In this dissociation of their melted salts the spectra of the alkaline metals differ from those hitherto described. Many of the lines become extended and diffused, others almost disappear. Practically, and especially in presence of the non-metals, the spectrum of sodium is reduced to three bright characteristic double rays, — $\text{Na}\delta$, $\text{Na}\alpha$ (Fraunhofer D), $\text{Na}\beta$, each blended into a single ray in a more prismatic apparatus. In potassium, the classical red rays, $\text{K}\delta$, situate at the extremity of the spectrum, are always very diffuse. The $\text{K}\gamma$, is very bright and characteristic. There are also, in the red, three very distinct rays: — $630\cdot8$, $624\cdot55$, $611\cdot75$. The brightest group is $\text{K}\alpha$, in the green, which gives the most sensitive reaction in the scale. Lithium has six rays, easily seen and very characteristic: — $670\cdot6$, strong and bright; $610\cdot3$, very strong; $497\cdot2$, strong; $460\cdot3$, strong, broad, diffused; $427\cdot3$, readily seen; $413\cdot2$, readily visible, but very diffuse.

A Reaction of the Cuprous Compounds which may serve to Characterise the Nitrites. — Paul Sabatier. — (See p. 6).

On the Zirconio-tungstic Compounds. — L. A. Hallopean. — The author describes a zirconio-decitungstate, $10\text{WO}_3 \cdot 3\text{ZrO}_2 \cdot 4\text{K}_2\text{O} + 15\text{H}_2\text{O}$; the dizirconio-decitungstate, $10\text{WO}_3 \cdot 2\text{ZrO}_2 \cdot 4\text{K}_2\text{O} + 20\text{H}_2\text{O}$; and the ammonium zirconio-decitungstate, $10\text{WO}_3 \cdot 5(\text{NH}_4)_2\text{O} + 11\text{H}_2\text{O}$.

Synthesis of Natural Methyl-heptenone. — Ph. Barbier and L. Bouveault. — Not suitable for abridgment.

Action of the Porcelain Filter upon the Poison of the Viper: Separation of the Toxic Substances from those which act as Vaccines. — C. Phisalix. — In the venom of the viper the "vaccinating" substances are distinct from the toxic matters, and may be separated by filtration (apparently with the Chamberland filter).

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 23.

Preparation of Methyl Nitrate. — M. Delépine. — The author adopts a modification of the Champion

process. He uses nitric acid of 36° instead of 48° , and adds at the conclusion sulphuric acid, which causes an almost instantaneous separation of the ether.

Nitro-Substitutions. — C. Matignon and M. Deligny. — The isomers of position have the same combustion-heats, excepting experimental arrows. In thermic researches it is sufficient to operate upon one of the three terms—the ortho, meta, or para. The differences oscillate around 45 calories, and are almost independent of the function of the substance in which substitution is effected. The generating equation of these ratio-compounds, deduced from the mean value of 45 cal., leads to a thermic liberation of $36\cdot7$ cal.

Condensation-products of Isobutyric Aldehyd. — G. Urbain. — It results from the reaction obtained that the isomer of dimethyl hexanalone has really the constitution which theory leads us to expect. The second part of this investigation gives the mechanism of the action (studied by Fossak) of concentrated alcoholic potassa upon isobutyric aldehyd.

Fission of Dioxystearic Acid. — P. Freundler. — It is certain that dioxystearic acid obtained by setting out from oleic acid is a racemic acid, a fact quite in accord with the theory of Guye. In dioxystearic acid two of the masses are very heavy, and must attract the centre of gravity of the tetrahedron towards the edge which connects them, and consequently towards the primitive plane of symmetry.

Certain Chlorated Ethers. — P. Freundler. — This extensive memoir does not admit of useful abstraction.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. i., No. 3.

Report presented in the name of the Committee of Chemical Arts on the Labours of M. Effront. — The authors explain the results which M. Effront has obtained by introducing fluorides into the industries of fermentation.

Manufacture of Linoleum. — Walter F. Reid. — From the *Journal of the Chemical Society*.

Part Played by Alumina in the Production of Glass. — From the *Comptes Rendus*.

No. 4.

Report presented on behalf of the Committee of Economical Arts, by M. Violle, concerning a System of Gas-Burners devised by A. Bondsept. — The principle of the system consists in mixing intimately the coal-gas with air, at the very extremity of the burner. It is said to increase both the yield and the brilliancy of the Auer burner; but the manner in which this is supposed to be effected requires for its explanation the twenty-three accompanying figures.

Determination of the Essential Oils by means of Common Salt. — M. Kutscheroff. — This bulky memoir cannot be intelligibly reproduced without the five illustrations and the numerous accompanying tables.

Mechanical and Thermic Properties of certain New Glasses devised by Winkelmann and Schott, summarised by H. Le Chatelier. — The reporter holds that boric acid and zinc oxide, ingredients required in the glasses of the inventor, are not miscible in the proportions indicated.

Refuse Destructors. — Stevenson Macadam. — From the *Journal of the Chemical Society*.

A New Derivative of Cellulose. — Clayton Beadle and Arthur Little. — Apparently from the *Journal of the Franklin Institute*.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxiv., No. 1.

This number contains no chemical matter.

MISCELLANEOUS.

Appointment.—The Council of the Pharmaceutical Society, at its last meeting, appointed Dr. J. Norman Collie, F.R.S., to the Chair of Chemistry in the Society's School of Pharmacy. Dr. Collie has for some time been associated with Professor Ramsay in the teaching of Chemistry at University College, London, and is a prominent member of the Chemical Society.

Albert Medal.—The Albert Medal of the Society of Arts has been awarded, with the approval of H.R.H. the Prince of Wales, the President of the Society, to Professor David Edward Hughes, F.R.S., "in recognition of the services he has rendered to Arts, Manufactures, and Commerce by his numerous inventions in electricity and magnetism, especially the printing telegraph and the microphone."

International Exhibition at Baden.—An International Exhibition and Competition for Hygiene, Popular Nutrition, and provision for Armies, in connection with a Special Exhibition for Sport and Foreign Intercourse, opens at Baden-Baden on August 15th.

Tuberculosis in Goats.—A goat which had been considered as healthy, so that its milk had been consumed unboiled, was found to be affected with tuberculosis in both lungs. Hence the alleged immunity of goats to tuberculosis is refuted. This is the more serious as goats' milk has been recommended for the use of phthisical persons, and has been consumed unboiled.—*Chemiker Zeitung und Munchen Med. Wochenschrift.*

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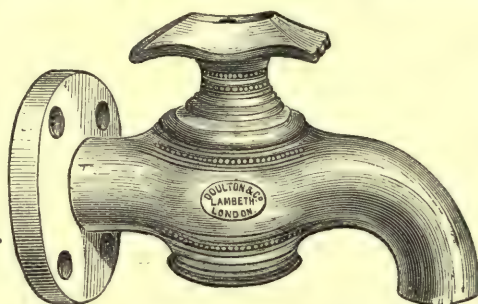
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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1911.

RESEARCHES ON THE METALLIC CARBIDES.*

By HENRI MOISSAN, Membre de l'Institut.

DEFINITE and crystalline combinations of carbon with metalloids and metals have as yet been very little known. It is only known that certain metals, such as iron, can dissolve carbon, giving rise to "cast" metals (*fontes*).

The knowledge that chemists possess on this point is the slighter inasmuch as these combinations are only produced at a very high temperature. The use I have made of the electric arc as a means of heating in the laboratory has enabled me to examine this question. In the present note I will give an account of my researches on this subject.

At the high temperature of the electric furnace certain metals, such as gold, bismuth, lead, and tin, do not dissolve carbon.

Liquid copper only takes up a very small quantity, sufficient, however, to change its properties and profoundly modify its malleability.

Silver at its boiling-point dissolves a small quantity of carbon, which it gives up on cooling in the form of graphite. This cast silver, obtained at a very high temperature, possesses the curious property of increasing in volume when passing from the liquid to the solid state. This phenomenon is analogous to what is met with in iron. Silver and pure iron diminish in volume when passing from the liquid to the solid state; on the other hand, cast iron and cast silver under the same circumstances increase in volume.

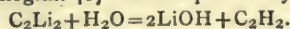
Aluminium possesses identical properties.

The metals of the platinum group at their temperatures of ebullition dissolve carbon with facility, and abandon it in the form of graphite before they solidify. This graphite is abundant.

A large number of metals, on the other hand, at the temperature of the electric furnace produce definite crystalline compounds.

In 1836 Ed. Davy showed that potassium could unite with carbon and produce a compound decomposed by water with evolution of a new hydrocarbon. It was thus that this *savant* discovered acetylene, the synthesis of which was later on effected by M. Berthelot.

On heating a mixture of lithia or carbonate of lithia and carbon in my electric furnace, I have obtained with facility carbide of lithium in transparent crystals, disengaging per kilogram. 487 litres of pure acetylene gas,—

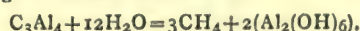


In the same way, by heating in my electric furnace a mixture of an oxide and carbon, I have been the first to obtain by a general method, in the pure crystalline state, and in notable quantities, the carbides of calcium, barium, and strontium. The carbide of calcium had already been prepared in the form of a powder, black, amorphous, and impure. Without going into the history of the subject, I may recall the researches of Wöhler, of M. Maquenne, and those of M. Travers on this subject.

All these carbides are decomposed on contact with pure water with disengagement of acetylene. The three alkaline-earth carbides have a formula corresponding to C_2R , and carbonate of lithium to the formula C_2Li_2 . The industrial preparation of acetylene is founded on this reaction.

Another type of carbide, crystallising in hexagonal plates, transparent, and of a centimetre in diameter, is

furnished by aluminium. This metal strongly heated in the electric furnace in the presence of carbon is filled with yellow plates of carbide, which may be isolated by a sufficiently delicate treatment, by means of a weak solution of hydrochloric acid cooled to the temperature of melting ice. This metallic carbide is decomposed by water at the ordinary temperature, furnishing alumina and pure methane gas. It has the formula—



My assistant, H. Lebeau, has obtained under the same conditions carbonate of glucina, which also furnishes, in cold water, pure methane.

The metals of the cerite group have given us crystalline carbides, the formula of which is similar to that of the alkaline-earth carbides, C_2R . We have specially studied the decomposition by water of the carbides of cerium, C_2Ce , of lanthanum, C_2La , of yttrium, C_2Y , and of thorium, C_2Th . All these bodies decompose water, yielding a gaseous mixture rich in acetylene and containing methane. With the carbide of thorium the acetylene diminishes and the methane increases.

None of our experiments with iron have given us definite crystalline compounds. At the ordinary pressure and at a high temperature iron has never furnished a definite compound.

It has long been known, thanks to the researches of MM. Troost and Hautefeuille, that manganese gives a carbide, CMn_3 . This carbide may be prepared with the greatest ease in the electric furnace, and in contact with cold water it yields a mixture of equal volumes of methane and hydrogen,—



Carbide of uranium, C_3U_2 , which I have obtained by the same methods, gives a more complex reaction; the carbide, well crystallised and transparent when in thin pieces, is decomposed in contact with water, yielding a gaseous mixture containing a large quantity of methane, of hydrogen, and of ethylene. But the most interesting fact about this carbide is the following:—The action of cold water not only produces gaseous hydrocarbons,—it forms in abundance liquid and solid hydrocarbons. Two-thirds of the carbon in this compound is recovered in this form.

The carbides of cerium and lanthanum, by their decomposition in water, have also furnished us with liquid and solid hydrocarbons, but in small quantity.

All these carbides, decomposable by water, at the ordinary temperature, with production of carburetted hydrogens, constitute the first class of compounds of the family of metallic carbides.

The second class is furnished by the carbides which do not decompose water at the ordinary temperature, such as the carbides of molybdenum, CMo_2 , of tungsten, CW_2 , of chromium, CCr_4 and C_2Cr_3 . These latter compounds are crystalline and non-transparent, with metallic lustre. They possess great hardness, and only fuse at a very high temperature. We have prepared them all in the electric furnace, and have given the detail of the experiments, together with all the analyses, in the *Comptes Rendus de l'Académie des Sciences de Paris*.

The metalloids have also furnished with carbon, at the temperature of the electric furnace, crystalline and definite compounds. We may mention, for example, the carbide of silicon, CSi , discovered by Mr. Acheson, and prepared to-day in commerce under the name of carborundum; the carbide of titanium, CTi , the hardness of which is sufficient to scratch diamond; the carbide of zirconium, CZr ; and the carbide of vanadium, CVa . We have described the preparation and properties of these new carbides.

One general fact is noticeable in the numerous researches which I have undertaken with the electric furnace:—The compounds produced at a high temperature have always a very simple formula, and most frequently

* A Paper read before the Royal Society.

there only exists one combination. But the most curious reaction brought to light in these researches is the easy production of hydrocarbons, gaseous, liquid, or solid, by the action of cold water on certain of these metallic carbides. It seems to us that these studies should have a certain interest for geologists. The disengagement of more or less pure methane which is met with in certain localities, lasting for ages, may have its origin in the action of water on carbide of aluminium.

Starting from 4 kilograms of carbide of uranium, we obtained in one experiment more than 100 grms. of liquid hydrocarbons. The mixture thus obtained is composed in great part of non-saturated ethylenic carbides, and a small quantity of acetylenic carbides. These carbides are produced in the presence of a large proportion of methane and hydrogen at the atmospheric pressure and ordinary temperature: this leads us to think that when the decomposition takes place at an elevated temperature there will be produced saturated hydrocarbons analogous to petroleum. M. Berthelot has, in fact, established that the direct fixation of hydrogen on a non-saturated hydrocarbon may be effected by the sole action of heat.

The existence of these new carbides destructible by water may therefore modify the theoretical ideas which have been hitherto advanced to explain the formation of certain petroleum or other carbonaceous products. It is very certain that we must guard ourselves against too hasty generalisations. It is probable that there exist petroleum of different origins. At Autun, for instance, the bituminous schists certainly appear to have been formed by the decomposition of organic matters. On the other hand, in the Limagne, the asphalt impregnates all the fissures of an Aquitanian limestone which is very poor in fossils. This asphalt is in direct relation with the veins of peperite (basaltic tuff), and consequently in evident relation with the volcanic eruptions of the Limagne.

A boring recently made at Riom, at 1200 metres depth, led to the flow of several litres of petroleum. The formation of this liquid hydrocarbon in this locality may be attributed to the action of water on metallic carbides.

In connection with carbide of calcium we have shown that under some conditions this compound may burn and give rise to carbonic acid. It is probable that, in the earliest geologic times, nearly all the carbon on the earth existed in the form of metallic carbides. When water intervened in the reactions the metallic carbides have given rise to hydrocarbons, and, by oxidation, to carbonic acid. We may find an example of this reaction in the environs of St. Neaire. The granites which in this place form the edge of the tertiary basin give off continuously, and in great quantity, carbonic acid gas.

We also think that certain volcanic phenomena may be attributed to the action of water on easily decomposable metallic carbides. All geologists know that the last manifestation from a volcanic centre consists of very varied carbonaceous emanations, ranging from asphalt and petroleum to the ultimate term of all oxidation, carbonic acid.

A movement of the earth causing the contact of water and metallic carbides may produce a violent disengagement of gaseous masses. As the temperature rises the phenomena of polymerisation of the carbides intervene to furnish a long series of complex products. The hydrocarbons may thus be at first formed. The phenomena of oxidation appear to follow and complicate the reactions. In certain places a volcanic fissure may act as a powerful draught chimney. It is known that the nature of the gas collected in the fumaroles varies according as the volcanic centre is immersed in the ocean or surrounded with atmospheric air. At Santorin, for instance, M. Fouqué has collected free hydrogen in the submerged volcanic vents, while in the land fissures he only detected aqueous vapour.

The existence of these metallic carbides, so easy to prepare at high temperatures, and which may probably be

encountered in the deeper strata of the globe,* enable us therefore to explain in some cases the formation of liquid or solid hydrocarbons, and the cause of certain volcanic eruptions.

THE ESTIMATION OF NICKEL IN STEEL, &c.

By H. BREARLEY.

THE well known instructions for separating iron from manganese, nickel, &c., by precipitating with sodium or ammonium acetate are:—Solution must be neutral, with slight turbidity, or solution must have only a few drops of acid in excess.

In separating Ni in this way it was noticed that if, after clearing up the slight turbidity with HCl, the addition of acid was continued, the brown red colour disappeared, and the solution had the lemon colour usually possessed by iron solutions when much free HCl is present. I was surprised to find that with this somewhat large excess of free acid the iron could be precipitated by ammonium or sodium acetate; and, moreover, the percentage of Ni separated in one precipitation was greater than could be obtained with ordinary neutralisations. Even beyond this straw colour, as much as 1 c.c. strong HCl could be added when operating on 500 c.c. of solution, and under such circumstances the Ni separation was almost complete in one precipitation. With so large an excess of free acid, the ferric acetate readily re-dissolved as the solution cooled, and the results obtained were not strictly uniform unless 2 or 3 c.c. of acetic acid were also present. This led me to see if a large excess of acetic acid with only a slight excess of HCl would give satisfactory results. It turned out to be better than the HCl, and I found that as much as 100 c.c. strong acetic acid could be added before the acetate precipitation when operating on 1 litre of solution; 50 c.c., however, will give an absolute separation of Ni and Fe.

These facts may have been previously noticed. They were, however, unknown to me, and no book on steel analysis I am acquainted with ("Select Methods," Blair, Arnold, &c.) gives instructions very dissimilar to those noted at the beginning of this article.

The method based on these facts is as follows:—

Weigh 1 grm. of steel into an 1100 c.c. beaker, dissolve in 20 c.c. HNO₃ (1·20), cool somewhat; add dilute ammonia to slight precipitation, and then HCl until it quite disappears; add 70 c.c. strong acetic acid, hot water to 950 c.c. or so, 50 or 70 c.c. ammonium acetate, and boil. Make up to 1000 c.c., and filter off one-half the solution. Transfer to a large flask and cool, make faintly but distinctly alkaline with ammonia, add 2 c.c. KI and 2 c.c. AgNO₃. Iodide of silver is formed in the solution; now run in standard potassium cyanide until the AgI dissolves, and the solution is as crystal clear as it was before the silver nitrate was added.

The KCN is standardised as follows (since it alters its strength from week to week it should be standardised every few days):—

To the clear solution of the titrated sample 10 or 20 c.c. of standard Ni is added and titrated with KCN. We thus know the value of 1 c.c. KCN in terms of nickel. Several indicators are now added to the clear solution and titrated, and thus the KCN necessary to dissolve one AgI indicator is found. The necessary calculations need no further explanation. It is better to standardise on the sample solution, so that the KCN may be measured under identical conditions in each case.

Here are some results on ordinary steel to which definite quantities of the standard nickel had been added:—

* The difference between the mean density of the earth and that of its superficial crust appears to point to the existence of a central mass rich in metal. The existence of metallic iron meteorites strengthens this hypothesis.

Nickel added. Per cent.	Nickel found. 70 c.c. acetic.	100 c.c. acetic used.
1	1'003	1'003
2	1'990	1'988
3	3'000	—
4	3'992	4'014
5	4'996	5'004

A sample of steel sent from the works gave 5'1 per cent nickel. We were subsequently informed that the sample had been most carefully prepared, and the maximum theoretically present was 5'146 per cent.

The accuracy of the method is undoubted, and when a number of estimations are to be made the time required does not exceed thirty minutes. I propose to note a few points which greatly enhance the rapidity of the estimation, and to show that they introduce no inaccuracy.

Hot Water for Filling up.—Many books state that the solution must be cold before the acetate is added. This is probably because the iron comes down at a low temperature when no excess of acid is present. With 70 to 100 c.c. free acetic acid, the precipitate does not appear before 85–90° C. If the precipitation occurs immediately on the addition of acetate the results are low; e.g., boiling water was added to two samples containing 3 per cent Ni, precipitation followed almost instantaneously, and the results were 2'92 and 2'91 per cent; but two other samples which came down on heating for one to two minutes gave 3'01 to 3'00 per cent.

Filtration.—At first I filtered through fluted English papers. It was always necessary to filter until the pores of the paper had become stopped somewhat, and during this time the solution was getting cold, and not unfrequently re-dissolving some of the ferric acetate, as it will do if the temperature falls below the point of formation. The time required was from 5 to 10 minutes. I now use a funnel whose stem is horizontal at the tip, place a perforated plate (1½ inches diameter) therein, and cover with a layer of fibrous asbestos, such as is used for filtering carbons and used with the Gooch crucible. The under side of the plate and the stem of the funnel must be filled with water. After the solution is made up to 1000 c.c. it is returned to the beaker and kept well wrapped in dusters. In ten or fifteen minutes nearly all the iron has settled. About 60 c.c. is poured on to the asbestos and allowed to run through. This is repeated until about 300 c.c. is passed; by this means the water is completely driven from the asbestos and stem. The next 500 c.c. is collected for titration. The total filtration does not take more than a minute. That the above method of filtration introduces no inaccuracies may be readily seen by supposing each 60 c.c. mixes with the water in funnel, for instance. A filter made with strong HCl in this way gave only a slight opalescence with silver nitrate after the passage of the last 60 c.c.

Influence of Special Elements.

Tungsten may be separated by solution in aqua regia, evaporating to dryness, filtering off WO_3 , and proceeding with filtrate as usual; but it occasions little difficulty to proceed as though no W was present.

Manganese.—The Mn is separated along with the Ni; it exerts no influence on the titration, as may be seen:—

Mn present.		Ni found.	
1'65 p.c.	2'03 p.c.	1'65 p.c.	2'03 p.c.
Ni added	nil	nil	nil
" "	2 p.c.	2 p.c.	2'008 p.c.

Chromium gives to the filtrate a pinky colouration; this turns light brown when the solution is made alkaline, and though no precipitate appears, the slight opalescence towards the end of the reaction is more easily overlooked than in a colourless solution. If the iron precipitate is boiled for half an hour the filtrate is colourless, and the filtration occasions no difficulty.

Copper cannot be separated by means of lead, zinc, aluminium, &c., without in turn needing to be separated themselves, because they react in the final titration. It may be precipitated by means of H_2S or sodium hyposulphite in an acid solution just after dissolving. A more expeditious way, however, is to proceed as usual, and then to the filtrate containing Ni and Cu add excess of H_2SO_3 and 5 c.c. KCNS, 2 per cent solution (Crookes, "Select Methods," 3rd ed., p. 294). Slightly better results are obtained by adding 25 c.c. dilute ammonia (3 to 1) to neutralise about half the free acid. The precipitated subsulphocyanide is filtered through asbestos. The precipitate has a tendency to run through on washing; it is therefore advisable to measure the quantity filtered through and measure the quantity retained in the funnel stem and asbestos, and make the necessary correction, always remembering that the nickel solution in the funnel has displaced an equal volume of water with which the asbestos filter was made. The excess of H_2SO_3 affects the titration but very slightly, if at all; but if pure KCNS is not obtainable, a blank estimation should be made. Some estimations made in this manner gave:—

Cu added. Per cent.	Ni added. Per cent.	Ni recovered.
1	2	1'981
1	2	1'978
3	2	1'968
*2	2	1'970

* Was made with KCNS containing KCN.

Particulars of Reagents.

Ammonium Acetate.—Made by neutralising acetic acid with ammonia. Approximately 580 c.c. acetic acid and 180 c.c. ammonia.

Potassium Cyanide.—4½ grms. per litre.

Standard Nickel.—Cube nickel contains about 99'5 per cent pure nickel. So much as equals 1 gm. pure nickel is dissolved in small quantity of nitric acid and made up to 1 litre. If the Ni contains much iron it should be separated with ammonium acetate, &c.

Silver Nitrate.—2'5 grms. per litre.

Potassium Iodide.—20 grms. per litre.

Preliminary experiments have been made with a view of separating other metals from iron in this way. I hope to report progress shortly.

The Laboratory, Norfolk Works, Sheffield.

ARSENATE OF LEAD, A NEW INSECTICIDE.*

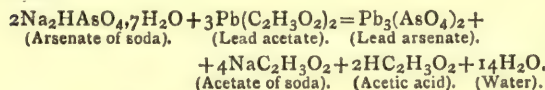
By FRANK T. SHUTT, M.A., F.I.C., F.C.S.

THIS substance has been recommended as a substitute for Paris green in spraying mixtures used for the destruction of "biting" insects, such as the apple worm (Codling Moth) and the Plum Curculio. Being insoluble in water, and reported as non-injurious to foliage, it is held that it may with safety be employed in larger amounts than those given in the formulæ containing Paris green; at the same time it is said that this compound is equally as efficacious in the extermination of insect foes as the latter well-known and widely used insecticide.

Since many erroneous and misleading formulæ have appeared in print for its preparation, it has been thought advisable to ascertain the exact chemical nature of the compound used, and to deduce therefrom the correct weight of the materials to employ, corroborating the latter by actual experiment. It is probable that some of the apparent discrepancies in the published formulæ have been due to the employment of crude and impure arsenate of soda, such as is used in calico-printing. The chemi-

* From the "Report on Experimental Farms to the Department of Agriculture, Canada."

cals used are acetate of lead and arsenate of soda, the result of the reaction on mixing solutions of these being the formation of an insoluble precipitate of lead arsenate, acetate of soda remaining in solution. Lead arsenate so formed is a white amorphous compound, settling to the bottom of the vessel on standing. The reaction when using pure reagents is represented by the following equation:—



Directions for Preparing the Insecticide.

To prepare fifty gallons of the mixture at the rate of one pound of lead arsenate to 200 gallons of water:—Dissolve 3 ounces of arsenate of soda in a quart or so of water (it dissolves readily in cold water). Dissolve $4\frac{1}{2}$ ounces of lead acetate in a similar volume of water. Pour both solutions into a barrel already containing about 45 gallons of water and stir well. The volume may now be made up to fifty gallons. This formula provides for the presence of a slight excess of lead acetate in solution; if the arsenate of soda were in excess, injury would probably result to the foliage.

The lead arsenate remains longer in suspension when precipitated in a large volume of water than when made concentrated and subsequently diluted.

On filtering off a little of the liquid and adding to it a few drops of the arsenate of soda solution (which is reserved for this purpose), a white precipitate should form, showing excess of lead.

It should be remembered that arsenate of soda and acetate of lead, as well as the product, are poisonous.

Respecting the price of the material, I could not obtain any Canadian quotations for commercial arsenate of soda; the pure article costs about \$2 per pound. Acetate of lead retails at 25 cents per pound, or in quantities of five pounds or more at 15 cents per pound. At these prices, the cost of the material for 50 gallons of the insecticide (strength as above) would be about 42 cents.

THE REDUCTION OF COPPER SULPHIDE.

By DELIA STICKNEY.

J. UHL, in his paper "Ueber Einwirkung von Schwefeldioxyd auf Metalle" (*Ber. d. chem. Ges.*, xxiii., 1215), speaks of reducing copper sulphide by heating it in a stream of hydrogen. A simpler way to accomplish the reduction is to let the compound come in contact with the flame of the ordinary Bunsen burner until a change in colour is seen. Copper sulphide, made by heating copper turnings and flowers of sulphur in an ignition-tube, was held by forceps in the flame for five or ten minutes. The bluish-black sulphide turned dark red, and the odour of sulphur dioxide was noticed. To determine whether this was metallic copper or cuprous oxide, the experiment was made on a larger scale. Copper sulphide, prepared in the usual way, was ground, and heated in a porcelain dish with the flame playing directly upon it. During the heating, the mass showed blue, green, and black colours, shades of red and of metallic copper, and under the lens many threads of bright copper were distinctly seen in the soft spongy mass. The unreduced part was hard and brittle, but the coloured parts were soft and friable. After successive grindings and heatings, very few hard lumps remained, but each time the mass felt softer under the pestle, and looked more like spongy copper.

To see if cuprous oxide was formed in any great amount, equal quantities of this product and of cuprous oxide were treated with concentrated hydrochloric acid; cuprous oxide dissolved entirely, but the other left a bright residue in the bottom of the tube. A test with ammonia showed

that but little had dissolved. The residue was taken out, dried upon filter paper, and examined under a lens. The greater part was bright copper, but there were also some particles of a dark colour, probably a little of the sulphide not reduced. Some of the product obtained by grinding and heating in this way was put into the flame of the blast lamp, and heated gradually until the copper melted. A little matte, tarnished on the outside, was formed in the bottom of the dish, which analysis showed to contain 97—98 per cent pure copper.

Experiments were now made with copper sulphide heated under different conditions. It was used just as it came from the tube, and heated undisturbed for one to four hours. The hard black mass gradually fell apart loosely, and formed the most beautiful product that had been obtained. Varying shades of red were seen, mixed with iridescent, bluish-black parts, arranged often in bands, and in the centre, and on the bottom, the little bright sheafs of metallic copper containing threads one-fourth to one-half inch in length were very abundant. To see if greater heat hastened the process, the sulphide was heated in the same way by the blast lamp. It melted a little on the edges, but remained a hard, brittle, grey mass with but little of the red colour on it, showing that the gentle reducing action of the Bunsen flame was needed rather than a high degree of heat.

Once the sulphide came from the tube in which it was made so hot that the free sulphur burned in the air. When the action was over, a few red spots were seen here and there. This suggested that a little free sulphur might hasten the reduction, and when the process was half completed, the addition of this seemed to shorten the time. Cupric oxide and cuprous oxide were intimately mixed with sulphur and heated, and here the reduction to copper was much quicker than in the case of the sulphide.

For the purpose of determining if contact with the flame was essential, some of the sulphide was heated for four to five hours in a porcelain crucible with the flame underneath, free contact with the air being allowed. Hardly any change in colour was seen. On the top was a slight reddish tinge, and a little sulphur was set free, but the mass was still hard and dark, keeping its shape. The form of the sulphide seemed to make no difference, for the results were the same whether it was powdered or in the form of filings or foil.

This easy method of reduction may be of use in general chemistry, as forming the complementary part of the familiar experiment with copper and sulphur, illustrating synthesis. The pupils' questions show always the desire to reverse the process, and get the copper back again.—*American Chemical Journal*, vol. xviii., No. 6.

THE CONDUCTIVITY OF SOLUTIONS OF ACETYLENE IN WATER.

By HARRY C. JONES and CHARLES R. ALLEN.*

KEISER (*Am. Chem. Journ.*, xiv., 285; and xv., 535) has shown by his work on the metallic compounds of acetylene, that both the hydrogen atoms possess acid properties, being capable of substitution by some metals. The compounds of silver and copper are formed by the substitution of two univalent metallic atoms for the two hydrogen atoms in the acetylene, and have the composition indicated by the formulæ Ag_2C_2 and Cu_2C_2 respectively. In these cases the acetylene conducts itself like a weak dibasic acid.

As the behaviour of acetylene in forming these compounds is that of an acid, it might be expected that it would exhibit, at least to some extent, the conductivity

* Solutions were prepared by Jones; the conductivity measurements were made by Allen.

phenomena shown by that class of substances. It appeared, therefore, that the investigation of the molecular conductivity of acetylene might be of interest.

For the cuprous acetylide, from which the acetylene was obtained, we are indebted to Prof. Keiser. The acetylene was liberated from the cuprous acetylide by heating it in a flask, on the water-bath, with a solution of potassium cyanide, as directed by Keiser. The gas was passed into water, which had been re-distilled from acid and alkaline potassium permanganate and condensed in a tube of block tin. The conductivity of the water used was determined and found to be negligible. This solution was tested for cyanogen, which might have passed over in some way, by boiling a portion of it with an alkali and ferrous sulphate, neutralising the alkali with an acid, and adding a ferric salt. No trace of a blue colour was obtained. The usual tests for copper, with ammonia or ammonium sulphide, also gave negative results, thus showing the absence of all possible impurities. Solutions of acetylene thus prepared and tested were used in the conductivity determinations.

Soon after the work was begun it was found that the solutions gave off the acetylene gas very rapidly, even in glass-stoppered bottles, and at temperatures only a little above zero. It was impossible to retain even dilute solutions at a constant concentration for any considerable time. After a number of trials, the following method was adopted as introducing the least error. The thermostat bath of the Kohlrausch-Ostwald conductivity apparatus was replaced by a vessel containing much finely-powdered ice and a little water, giving a temperature which was approximately zero. The acetylene solution of unknown concentration was cooled nearly to zero by placing it in a glass-stoppered bottle and immersing the bottle in a freezing mixture. A portion of this solution was then poured into the resistance cell (which was already in the ice-bath described above), and the position of equilibrium on the bridge determined as rapidly as possible. A known volume of the solution in the cell was then at once drawn off in a pipette, and the amount of acetylene present determined as follows:—A standard tenth-normal solution of silver nitrate and an exactly equivalent solution of potassium chloride were used. The gas was brought into combination by running in an excess of the silver nitrate solution. An equal volume of the potassium chloride solution was then run in, a few drops of a solution of potassium chromate, serving as an indicator, added, and the excess of potassium chloride titrated with the silver nitrate. As there was no loss of acetylene from the solution after the first addition of silver nitrate, the only loss of gas affecting the results was that which took place during the interval between the conductivity measurement and the first addition of silver nitrate, which was, on an average, only two or three minutes. Since the solutions of acetylene were very dilute, and the analyses, of necessity, made with a comparatively small volume, the standardisation of the solutions must be regarded as only roughly approximate. The results of the conductivity measurements of the acetylene solutions are given in the following table. The column headed v gives the volume in litres, which contains a one-half grm.-molecular weight of the gas; μv are the molecular conductivities at the volumes v .

	v .	μv .
1.	417	29'0
2.	833	41'0
3.	1111	50'0
4.	2502	77'0

Although these results are necessarily affected by considerable error, due to the causes indicated above, yet they undoubtedly show that solutions of acetylene in water are somewhat dissociated, and that this dissociation increases with the dilution—results which would be expected from the weakly acid character of the compound.

—*American Chemical Journal*, xviii., No. 5.

RESEARCHES ON THE RÖNTGEN RAYS.*

By ALFRED M. MAYER.

(Concluded from p. 8).

3. *The Formulæ of Transmission of the Röntgen Rays through Glass, Aluminium, Platinum, Green Tourmaline, and Herapathite.*

THE Röntgen rays, after their transmission through various substances, produce actinism on a photographic plate, and by the degree of this actinism we have attempted to obtain the formula of transmission peculiar to each substance. This action of the X rays is cumulative and evidently is entirely different from the transmission of light and radiant heat where the maximum of transmission is instantly reached and under proper and controllable conditions remains constant and therefore can be accurately measured. But with the X rays the amount of their action on the plate varies directly as the time of their action (see 4), depends on the distance of the sensitive plate from source of radiation, and on the energy of the source. Therefore this method of determining the constants of the formulæ of transmission of the X rays is somewhat arbitrary; but the exact conditions in the determination of the constants having been given, these conditions can readily be obtained by other experimenters. Thus, to have the same conditions as existed in our experiments, one has only to place a pile of crown glass plates 5'5 m.m. thick, at such a distance from the radiant source that on two hours' exposure the X rays will have just not visibly acted on the photographic plate after having traversed the glass. Some assumption has to be made as to the nature of the X rays, otherwise no progress can be made in determining the constants of their formulæ of transmission. We have assumed that they are homogeneous. The formulæ, as determined, hold good till they have conclusively been shown not to be homogeneous, which is very likely to happen in the progress of research on their nature.

The method used owes whatever merit it may have to the use of the wire netting devised by Professor Rood to give accurate indications of the relative permeability of various substances to the X rays. This wire netting he places on the slide covering the sensitive plate, and on the netting he places substances of various thickness. The netting completely screens the X rays, and its image on the negative is the brightest possible to obtain in the given conditions. If a plate of a substance should also entirely screen the X rays, then the image of the netting is invisible in the photograph of this substance, and as plates of substances allow more and more of the X rays to traverse them, the images of the netting in the photographs of these substances are more and more bright. If the image of the netting in the photographs of two substances should be equally bright, then these two plates transmit equal actinic action to the sensitive plate. Thus this ingenious device serves as a very delicate photometer in determining the fact just mentioned.

It occurred to me that the wire netting could also give me data with which to determine the constants of the formulæ of transmission of the X rays through various substances. The method devised is as follows:—On a wire netting with 8 meshes to the inch placed on the slide of the plate holder, are cemented piles of glass discs (each glass about one-tenth m.m. thick); these piles gradually increase in thickness. These piles of glass were exposed to the action of the X rays, so that the photographic plate was 25 c.m. distant from the radiant source. In the apparatus used this distance could be accurately measured. After an exposure of two hours it was found, on developing the plate, that the netting was just visible in the photograph of the pile 5'35 m.m. thick, and that it was not visible in

* From the *American Journal of Science*, vol. i., June, 1896.

the photograph of the pile 5.5 m.m. thick. In this last case, though the X rays had penetrated to the sensitive film, yet the difference in the screening effect of the netting and of the glass was not visible, because the eye cannot distinguish between the illumination of juxtaposed surfaces which differ in illumination by about $\frac{1}{100}$. Hence, through the last pile of 5.5 m.m. about $\frac{1}{100}$ of the actinic intensity of the incident beam had passed.

Now the formula of transmission of rays through a substance which does not reflect these rays is $I' = Ia^t$. Where I' = the intensity of the transmitted beam; I = the intensity of the incident beam; a = a constant depending on the substance, and t is an exponent of a , and t is the thickness of the substance. We have taken one-tenth m.m. as the unit of t .

From the conditions of the experiment, $I' = Ia^t = \frac{1}{100}$, and as t is known, a is readily computed. The accuracy of the determination of a depends on the value of the least perceptible difference in illumination that the eye can distinguish in two juxtaposed surfaces. We have adopted $\frac{1}{100}$ as the most probable value.* But suppose that the fraction is not $\frac{1}{100}$, but $\frac{1}{110}$, or $\frac{1}{90}$, then the departure of these fractions from $\frac{1}{100}$ will affect the constant by 4 units in the third decimal place.

These experiments, made in the conditions we have indicated, give for the formula of transmission through the glass used, a crown glass made by Chance and Co.,—

$$I' = I \times 0.92^t.$$

Having this formula as a basis, it is comparatively easy to determine the constants of another substance, by placing the substance on the netting with piles of glass of graded thickness and exposing them to the X rays. We then see what thickness of glass gives the same illumination to the image of the netting as does the known thickness of the substance. Thus, the netting in the photograph of a disc of herapathite 0.9 m.m. thick had the same brightness as in the photograph of a pile of glass 0.69 m.m. thick. By the formula, glass 0.69 m.m. thick transmits 0.5636 of the incident beam, and herapathite of 0.9 m.m. transmits the same. From this we compute that $I' = I \times 0.9382^t$ is the formula for the transmission of the X rays through herapathite, which for $t = 0.69$ gives 0.5636 of transmission.

In the same manner it was found that—

M.m.		M.m.
2.05 of aluminium	transmits the same as	2.44 of glass.
0.02 „ platinum	„	2.9 „
2.0 „ green tourmaline	„	2.0 „
0.69 „ herapathite	„	0.9 „

From these determinations we have computed the formulae of transmission of these substances.

Glass	$I' = I \times 0.92^t$
Aluminium	$I' = I \times 0.905^t$
Platinum	$I' = I \times 0.00063^t$
Green tourmaline	$I' = I \times 0.92^t$
Herapathite	$I' = I \times 0.938^t$

Taking the amount of transmission through aluminium of one-tenth m.m. and of 1 m.m. as unity, we have, in the following table, the relative transmission through the substances experimented on.

	$t = \frac{1}{10}$ m.m.	$t = 1$ m.m.
Aluminium	1	1
Glass	1.016	1.180
Green tourmaline	1.016	1.180
Herapathite	1.036	1.435
Platinum	0.000696	—

Platinum 0.06 m.m. thick is practically impervious to the rays from the Crookes tube used, transmitting only 0.005 of incident beam.

This method of determining the transmission of the X rays through various substances may be criticised, because in the experiments I obtain not alone the transmission through the substances placed on the slide of the plate-holder, but at the same time the transmission through the slide itself. If the slide has a measurable transmission, or, screening effect, then its equivalent in thickness of the substances placed on it should be added to them. This criticism, however, is nought, because experiments have shown that if the thickness of a portion of the slide is doubled by placing on it a piece of the material of which it is made, no screening of the X rays by this piece can be detected.

4. The Actinic Effect of the Röntgen Rays varies inversely as the square of the distance of the sensitive plate from the radiant source.

The slide covering a photographic plate had on it the wire netting, and the plate was exposed for 30 minutes to the X rays at a distance of 10 inches from the radiant source. Another similar plate in the same plate-holder was exposed for two hours at a distance of 20 inches from the radiant source. These distances could be accurately measured in the apparatus used. These plates were taken from the same box and developed side by side in the same tray. Indeed all the conditions were carefully made the same in the two experiments except the distance of plates from the radiant source. On developing the images on the plates they were exactly alike; the image of the netting had the same illumination on each plate, and the density of the films was the same. This experiment shows that the X rays act on a sensitive plate according to the law of the inverse squares.

From this law it follows that the actinic power of the X rays is not sensibly absorbed in traversing the air; also, that these rays are not sensibly diffused by radiation from the molecules of the air they traverse, the air being at ordinary barometric pressures.

These deductions, which necessarily follow from the law of the inverse square, are, however, at variance with the facts observed by Professor Pupin, who states, in *Science* of April 10, 1896: "There was evidently a diffuse scattering of the X rays in their passage through the air." "These experiments prove, beyond all reasonable doubt, that the Röntgen radiance is diffusely scattered through bodies, gases not excepted." These opinions of Professor Pupin are founded on experiments on the action of the X rays on a fluorescent screen, or, rather on a "fluoroscope," not on experiments on their actinic effects. In the latter case I am confident that the X rays act according to the law of the inverse squares, and therefore are not sensibly diffused. In the former case Professor Pupin finds that they are diffused in traversing the air, and very sensibly diffused if I understand aright his paper; but as he does not give any photometric measures, or estimates, of the intensity of the fluorescence in the geometric image of the slit, and outside of this image, one cannot form an opinion of the amount of the diffusion he describes. The facts of diffusion described by Professor Pupin are opposed to those discovered by so distinguished and experienced a physicist as Röntgen, who, in section 10 of his first paper, writes: "I find, using a Weber's photometer, that the intensity of the fluorescent light varies nearly as the inverse squares of the distance between screen and discharge tubes. This result is obtained from three very consistent sets of observations at distances of 100 and 200 m.m. Hence air absorbs the X rays much less than the cathode rays. This result is in complete agreement with the previously described result, that the fluorescence of the screen can be observed at 2 metres distance from the vacuum tube." Röntgen does not mention any diffusion observed by him in these experiments, and it is certain that he would have mentioned the existence of diffusion in experiments made to determine a law of

* "Photometric Experiments," O. N. Rood (*American Journal of Science*, July, 1870).

radiation, and which diffusion necessarily would have invalidated the law of inverse squares.

The radiation from the Crookes tube, used in the experiments described in this paper, came from a calcined shell supported by the anode wire and placed opposite the cathode. The tube was not sensibly heated during the experiments and the actinic power of its radiation remained constant. It was proved by taking a pin-hole photograph of the naked tube, with an exposure of two hours, that by far the larger proportion of the X rays emanated from a 4 m.m. square surface of the shell which was acted on by the cathode rays. The walls of the glass tube, as was proved by other independent photographic experiments, furnished a small percentage of X rays, but not enough to make their presence known in the pin-hole photograph, which had furnished quite a dense image of a portion of the shell. Furthermore the X rays from the glass wall itself were cut off and prevented from reaching the photographic plate by a diaphragm of lead with a circular opening of one-half inch, and at one inch distant from the radiant source. It is also to be remarked that this second source of the X rays was nearer to the photographic plate only by 7-10ths inch minus 0.06 inch, the thickness of the tube, hence any effects due to them may be neglected, as indeed the results in the experiments on the inverse squares show.

The experiments described in this paper were made in the private laboratory of Professor Rood in Columbia University. Professor Rood not only gave me the use of his apparatus, which he had made the subject of a special investigation before investigating with it, but he also gave me the advantage of the experience obtained during his researches on the X rays.

ON THE CALCULATION OF THE CONDUCTIVITY OF MIXTURES OF ELECTROLYTES HAVING A COMMON ION.*

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In a paper read before this Institute some months ago, Prof. MacGregor (*Trans. N. S. Instit. of Science*, ix., 101) showed how to obtain, by a graphical process, from observations of the electrical conductivity of a sufficient number of simple solutions of two electrolytes having a common ion, the data necessary for the calculation of the conductivity of a solution containing both electrolytes, according to the dissociation theory of electrolytic conduction; and in order to test this theory, he calculated the conductivities of a series of mixtures of solutions of sodium chloride and potassium chloride, which had been measured by Bender. He found that for dilute solutions his calculations agreed with Bender's observations within the limits of experimental error; but that, as the strength of the solution increased, the differences became larger, until, with a mixture of solutions containing each 4 gramme molecules per litre of salt (the strongest solutions with which Bender worked), a difference of 3.6 per cent was found. The method of calculation assumed that the ionic velocities of the constituent electrolytes were not changed by the mixing, and Prof. MacGregor attributed the differences between the calculated and observed values to the change which, as he pointed out, would probably be produced, in these velocities, by mixture.

At his suggestion I have made the observations described in this paper, with the object of determining (1) what the differences between the observed and calculated values are, in the case of mixtures of sodium and

potassium chloride solutions, of greater strength than those examined by Bender, and (2) how the calculated and observed values are related, in the case of solutions containing sodium chloride and hydrochloric acid,—electrolytes whose ionic velocities differ from one another much more than those of sodium and potassium chlorides.

The expression for the conductivity of a mixture of equal volumes of solutions of two electrolytes, 1 and 2, which contain n_1 and n_2 gramme-equivalents per unit of volume respectively, the ionisation coefficients of which, in the mixture, are α_1 and α_2 , the molecular conductivities of which at infinite dilution are $\mu_{\infty 1}$ and $\mu_{\infty 2}$, and which so change in volume on mixing that the ratio of the volume of the mixture to the sum of the volumes of the constituent solutions is β , is—

$$c = \frac{1}{2\beta} (\alpha_1 n_1 \mu_{\infty 1} + \alpha_2 n_2 \mu_{\infty 2}).$$

In order to calculate the conductivity of such a mixture, therefore, the seven quantities in this expression must be known. The ionisation coefficients, α_1 and α_2 , are determined by the graphical process referred to above, from series of observations of the conductivities of simple solutions of the constituent electrolytes. The conductivities at infinite dilution are determined by similar observations with very dilute solutions. The concentrations may be determined by analysis, and the quantity β by density measurements.

I intended at the outset to determine all these quantities myself, in order that the data of calculation might apply to exactly the same electrolytes. But owing to the fact that the electrolytic cell, to be used in the determination of conductivities at infinite dilution, although ordered months ago, did not arrive in time, I am compelled to use Kohlrausch's values of the conductivities at infinite dilution for the electrolytes examined.

Determination of Conductivities.

Kohlrausch's well-known method with the telephone and alternating current was used. The apparatus was supplied by Queen and Co., of Philadelphia, and consisted of a German silver bridge-wire, about 3 metres long, wound on a marble drum. The wire was divided into 1000 parts, and had a resistance of about 1.74 ohms. I calibrated it by the method of Strouhal and Barus (*Wied. Ann.*, x., p. 326, 1880), and applied the corrections thus determined to the measured resistances. (The greatest correction that had to be applied during the experiments was one division).

Four coils, marked 1, 10, 100, 1000 true ohms, formed part of the apparatus, and were guaranteed correct to 0.1 per cent. The range of the resistances measured during the experiments, however, was so small that I needed to use only one of these coils (that of 100 ohms). Hence it was not necessary for me to test the relative accuracy of the coils. Nor did I need to test the absolute accuracy of the 100 ohm coil, as it was not necessary for me to express conductivities in absolute measure.

The cell used was a U-shaped one, with enlargements for the electrodes, of the kind shown in Ostwald's "Physico-chemical Measurements," p. 226, fig. 178. The cell and also the electrodes (each of which had an area of about 7 sq. c.m.), were smaller than ordered, and the latter were so thin as to be easily bent. No change of resistance, however, could be noticed for small bendings of the plates, which could be readily detected by the eye and avoided. The induction coil was quite small, and had a specially rapid vibrator. It was kept in an adjoining room, that the noise might not disturb the operator; but after some practice it was found that measurements could be made without difficulty, even with considerable noise. Different kinds of batteries for working the coil were tried. The most satisfactory was found to be a small dry battery, made by the Mamisburg Electric Co., of the kind used for electric bells. With this apparatus the

* *Transactions of the Nova Scotian Institute of Science*, vol. ix., Session 1895-96.

"minimum" point on the bridge could be determined by the telephone to within $\frac{1}{4}$ division. This, at the centre of the bridge, meant a possible error of 0.2 per cent, and at the point of the bridge farthest from the centre, used in my experiments, a possible error of 0.3 per cent.

Temperature.

As the laboratory temperature varied considerably from day to day, the electrolytic cell was placed in a bath whose temperature was regulated by a thermostat of the kind described by Ostwald in his "Physico-chemical Measurements," p. 59. The resistances measured were so small that a sharp "minimum" was obtained when a water-bath was used. There was no necessity therefore for a petroleum-bath. The bath was stirred by a current of air from a small suction-pump, and the temperature kept as near to 18° C. as possible. When this temperature could not be exactly obtained, measurements of resistance were made at several near temperatures, and the temperature coefficients found. The coefficient was always about 2 per cent per degree.

The thermometer used was graduated to 0.1 degree centigrade, and could be easily read to 0.05 degree. This meant a possible error of 0.1 per cent in the determination of the resistance. The errors of the thermometer had recently been determined at the Physikalisch-Technische Reichsanstalt, Berlin.

The Platinising of the Electrodes.

The electrodes, after having been boiled in alkali and acid, were placed in a very dilute solution of chloroplatinic acid (H_2PtCl_6), and connected with a small battery, the direction of the current being frequently changed. When the electrodes had become covered with a black velvety coating, they were removed from the cell, and, in order to get rid of the chloroplatinic acid which adheres strongly to the platinum black, they were washed several times with boiling water. On one occasion, in the course of the experiments, the minimum point was found to be indistinct. The plates were accordingly replatinised, and distinctness found to have been regained. The experiments previously made (those on potassium chloride) may have been affected by a slight error due to defective platinising.

The Salts and Acids.

The potassium and sodium chlorides, obtained as chemically pure from Eimer and Amend, of New York, were further purified by re-crystallisation. Solutions of them were found to be neutral and free from sulphates and magnesia. Neither potassium nor other metals could be detected in the sodium chloride with the spectroscope. Sodium, but no other metal, could be detected in a flame coloured by the potassium chloride. The hydrochloric acid was obtained as chemically pure, and gave no residue on evaporation. It was free from sulphates.

The Water used.

The water was doubly distilled, with addition of sodium hydrate, in a tin-lined retort, and condensed in a block-tin pipe, the first part of the distillate being rejected. It was stored in bottles which had been used for this purpose for several years. It gave no residue when evaporated, was neutral, and gave no colour with Nessler's reagent.

Preparation and Analysis of the Simple Solutions.

The simple solutions were prepared by dissolving about the amount of salt required for the strongest solution, and subsequent diluting. The concentration in each case was determined by volumetric analysis. A solution of silver nitrate was used in estimating the chlorine in the potassium and sodium chlorides, and the amounts of salt present were calculated from the data thus obtained.

In making an analysis, 1 c.c. (or 5 c.c.) of the solution at 18° C. was drawn off by a pipette, placed in a flask, diluted, and coloured distinctly with neutral potassium

chromate. Silver nitrate standardised at 18° C. was run in from a burette, and a glass bulb filled with potassium chromate of the same shade as the solution being analysed was held before the eye. The end point by this means could be seen quite sharply.

A solution of ammonia was employed for estimating the hydrochloric acid, with cochineal as an indicator.

The pipettes and burettes used were tested by weighing the water which they delivered. They were found to be accurate to 0.1 per cent.

To determine the accuracy of the volumetric analysis, a solution of sodium chloride was prepared, containing a known quantity of the pure fused salt. The results of the analyses were found to be correct to 0.1 per cent.

Specific Gravity Determinations.

The object of specific gravity determinations was the finding of ρ in the above expression for the conductivity. For this purpose it was necessary to find the specific gravity to the third decimal place only. Hence the determinations were made with a Mohr-Westphal balance which read to the fourth decimal place, and might be trusted in the third.

In all the mixtures examined ρ was found to be practically equal to unity.

Preparation of the Mixtures.

A 50 c.c. pipette, which had been carefully washed, and stood on filter-paper for some time, was rinsed out several times with one of the constituents of the intended mixture, whose composition and specific gravity had been determined. The pipette was filled to the mark, and the solution run into a clean and dry bottle. The pipette was then washed, and the other constituent placed in the bottle as before, care being taken to use the pipette in exactly the same manner in both cases. All mixtures were made at 18° C., and the same pipette was used for both solutions, in order that the mixture might consist of exactly equal volumes of them.

The conductivities of solutions were found to increase on standing, which was doubtless due to portions of the glass being dissolved. The conductivities were therefore measured as soon after the solutions were made up as possible.

Capacity of the Electrolytic Cell.

To find the factor which would reduce the observed conductivities to the standard employed by Kohlrausch, viz., the conductivity of mercury at 0° C., the following simple solutions of potassium and sodium chloride were analysed, and their conductivities measured:—

Potassium Chloride.		Sodium Chloride.	
Concentration, (Grm.-molecules per litre.	Conduct- ivity, $\times 10^8$.	Concentration, Grm.-molecules per litre.	Conduct- ivity, $\times 10^8$.
2.07	1854	2.06	1199
2.61	2281	2.56	1517
2.94	2521	2.83	1616
3.26	2767	3.37	1786
3.68	3040	3.70	1876
3.88	3187	4.29	1970
		4.69	2025
		5.12	2087

These values were plotted on co-ordinate paper with concentrations as ordinates and conductivities as abscissæ, and smooth curves were drawn between the points so as to obviate accidental errors. Conductivities were taken off these curves and compared with the numbers given by Kohlrausch (*Wied. Ann.*, vi., 146) for solutions of equal concentration, as shown in the accompanying table (see next column).

It will be noticed that the ratios in the above table are not the same for all solutions, but are practically the same for solutions of both salts of the same conductivity. The

Concentration Grm.-molecules, per litre.	Potassium Chloride. Conductivity.		Ratio.
	Kohlrausch.	Observed.	
2	1728	1800	0.960
2.5	2122	2199	0.961
3	2480	2566	0.966
3.5	2822	2924	0.965

Concentration (Grm.-molecules per litre).	Sodium Chloride. Conductivity.		Ratio.
	Kohlrausch.	Observed.	
2	1209	1277	0.946
2.5	1412	1500	0.941
3	1584	1675	0.946
3.5	1728	1815	0.952
4	1846	1928	0.957
4.5	1935	2000	0.968
5	1991	2066	0.964

variation of the ratio may have been due to some unknown defect of apparatus or mode of using it; but as this source of error was equally operative in the case of solutions of both salts of the same conductivity, it would probably be equally operative also in mixtures of the same conductivity. Hence, in reducing the observed conductivity of a mixture of potassium and sodium chloride solutions to Kohlrausch's standard, the factor employed was the value of the ratio for the conductivity which the mixture was found to have, this ratio being determined from the above table by graphical interpolation. Bender found a similar variation in the ratio of his conductivities of solutions of these salts to Kohlrausch's conductivities for solutions of the same strength.

On comparing the observed conductivities of solutions of hydrochloric acid with conductivities of solutions of equal concentration, as given by Kohlrausch, the ratios were found to be practically uniform, and equal to 0.955. In the tables which follow all conductivities are expressed in terms of Kohlrausch's standard.

(To be continued).

NOTICES OF BOOKS.

Nitro-Explosives: a Practical Treatise concerning the Properties, Manufacture, and Analysis of Nitrated Substances, including the Fulminates, Smokeless Powders, and Celluloid. By P. GERALD SANFORD, F.I.C., F.C.S., Member of the Society of Public Analysts; Consulting Chemist to the Cotton-powder Company (Ltd.); late Resident Chemist at the Gun-cotton Works, Stowmarket, and the Dynamite Works, Hoyle, Cornwall. London: Crosby Lockwood and Son. 1896. Pp. 274.

THIS work, which may with full justice be styled a "practical treatise," confines itself to the nitro-explosives—a very numerous class of the High Explosives. The substances which have been nitrated include cellulose in its various forms, glycerin, benzene, starch, jute sugar, phenol, wood, straw, treacle, and horse-dung!

The "danger area" at works for the manufacture of explosives is that portion devoted to the actual manufacture or mixing of explosive materials. The author judiciously recommends that all "danger-buildings" should be made of wood, and that they should be surrounded by mounds of earth or sand. Formerly danger-buildings were made bomb proof, which in case of an explosion greatly augmented the danger. This arrangement had been adopted at the works in the Hartz, where Chapman was torn to pieces. In powder-mills it was formerly customary to surround the danger-buildings with

dense belts of trees. This precaution is utterly useless as against gun-cotton, dynamite, &c. With such agents the shock travels underground more rapidly than through the air. Thus at the great gun-cotton explosion at Stowmarket the windows of houses at some distance from the magazine were seen falling out of their frames before a sound was heard. The excellent caution is given that the clothing worn by the work-people upon the danger-area should have no pockets, which much reduces the chance of matches or steel articles being carried upon the danger-area. All tools used upon the danger-area should be of phosphor-bronze, and brass nails should be used not only in the erection of the building, but in the manufacture and closing of all packing-cases. As a matter of course the work-people change their shoes before entering a danger-building or the danger-area. The lightning-conductors, with which every danger-building and magazine should be fitted up, are of the construction proposed by Prof. Clerk-Maxwell.

Cordite, which has lately attracted considerable attention, is made at the Royal Gunpowder Factory at Waltham Abbey, and at one or two private factories; it consists of gunpowder 37 per cent, nitro-glycerin 58 per cent, and vaseline 5 per cent. A solvent, such as acetone, is added to effect the solution of the gun-cotton.

The acid mixture used in the manufacture of gun-cotton at Waltham Abbey consists of 3 parts by weight of sulphuric acid, sp. gr. 1.84, and 1 part nitric acid, of sp. gr. 1.52.

We are reminded that celluloid is a variety of cellulose, and that much care is required in its manufacture. Some years ago a large packet of celluloid combs exploded in the guard's van on a German railway.

Melinite seems to be little else than picric acid, but its exact formula is not known. It seems highly probable that the expectations held out concerning melinite were greatly exaggerated. The French military authorities are not known to have employed it in actual warfare.

All persons connected with the production and use of high explosives will find Mr. Sanford's work invaluable.

Les Actualites Chimiques. Review of the Progress of Pure and Applied Chemistry. (Appearing six times yearly). Published under the direction of Charles Friedel, of the Institute. Paris: George Carré.

OUR readers are, of course, aware that among our French neighbours the actual is not, as with us, the demonstrably existing, in contradistinction to the imaginary or the conjectural, but that which is at the present moment occurring or attracting attention as different from the past or the future.

Of the lectures or essays before us particular attention is due to the two first, that is, one by Prof. Schützenberger on the critiques of Dr. Hinrichs on the "Atomic Weights as determined by Stas" and that of Dr. Wyruboff on the "Periodic Classification of the Elements."

Dr. Hinrichs is pronounced here a mathematician rather than an experimentalist. His fundamental idea is that of the unity of matter. For him, and in some degree for all of us, the elements are the result of the condensation, according to certain laws, of a single principle which he names pentogen, and which we may identify with the *protyle* of the glorious friar Roger Bacon, and of Mr. W. Crookes in our own time.

This, Prof. Schützenberger says, is the theory of Prout in support of which Dumas brought forward his determinations. After the publication of the Memoir of Dumas the hypothesis of Prout seemed established. Yet Stas threw back everything into uncertainty. He put forward "determinations made with exceptional care, a minute criticism of the causes of error of which they admit, a precision which has never been reached before or since, and established with a certainty against which

it seemed difficult to contend that the atomic weights, far from being multiples of the same magnitude, as 0.5 or 0.25, have among themselves no single or rational relation."

Hinrich appeals from this judgment. He does not indeed criticise the material accuracy of the experiments of the Belgian chemist—a task, we may add, for which his aptitude is, to say the least, not proven—but he seeks to show that these beautiful experiments do not admit of the consequences which have been drawn from them.

The characteristics of the experiments of Stas are:—

1. The minute care introduced in the purification of the substances employed.

2. In operating upon large but variable quantities of matter. Thus, for lead he performed ten experiments, with quantities of lead varying from 103 to 250 grms.

For silver he effected 9 determinations, using doses of silver of from 77 to 404 grms.

Dr. Hinrichs argues that the mean of a series of experiments, the results of which differ from each other by small quantities, have not the chance of approaching nearer to the truth than any one of them. It is evident that if all the determinations are above, and unequally above, the truth, the mean will be less exact than the smallest number found.

In addition to the mathematical strictures of Dr. Hinrichs, he brings forward another kind, more intelligible to chemists.

Whenever we decompose, by heat, a compound which is thus resolved into a fixed and a gaseous or volatile constituent, it is extremely difficult to eliminate the last traces of the volatile product, a fraction of which remains energetically fixed on the non-volatile residue, and, although minimal, may be rendered sensible by delicate reactions. In support of this assertion we might cite very distinct observations controlled by a great number of experiments.

It is generally admitted that pure copper nitrate, if heated progressively to nascent redness, becomes pure cupric oxide as a fixed residue when every trace of nitrous vapour has disappeared. But if, after having heated such an oxide to dull redness for a long time in a current of air, we reduce it with hydrogen, it is always found that the weight of water formed is less than that which corresponds to the loss undergone by the oxide reduced to the state of copper, and that we calculate according to this loss on admitting that water is formed of 8 parts of oxygen and 1 part of hydrogen. This excess of loss undergone by the cupric oxide of the nitrate is due to nitrogen, which remains energetically fixed upon the product.

Hence it results necessarily that all the syntheses of water effected with the oxide of the nitrate give too high a value for the equivalent of oxygen with reference to $H = 1$, or too low a value with reference to $O = 16$.

With oxide of copper obtained by the direct combination of copper this discrepancy no longer exists.

Nothing proves that on the decomposition of potassium chlorate by heat the expulsion of the oxygen is absolute, so that what is calculated as potassium chloride does not retain obstinately a certain dose of oxygen. According to the great generality of facts of this kind, the inverse seems to us scarcely possible. Potassium chlorate, heated for a long time to nascent redness, until the cessation of all escape of gases, and even longer, gives with water a reaction of potassium chloride which, in presence of hydrochloric acid, decomposes extract of indigo in heat, and if it is thus the very foundation of the experiments of Stas is shaken, precise as they appear, and the entire edifice must be reconstructed.

When Stas transforms a known weight of pure silver into dry, and even fused, nitrate, and, from the weight of the nitrate found, deduces the atomic weight of nitrogen, we cannot exclude the suspicion that the residual nitrate may retain a fraction of the nitric acid used in excess to dissolve the silver, and that this residue in place of being NO_3Ag really represents NO_3Ag and δNO_3H .

If the cause of error which we thus point out is of a magnitude capable of seriously affecting the numbers found, there will be room to proceed to a revision. Perhaps we may then return to the theory of Prout and of Dumas.

We shall next proceed to consider the periodic classification of the elements.

Chemical Notes and Equations. By G. H. GEMMEL, F.I.C., F.C.S. London: Baillière, Tindall, and Cox. Edinburgh: Livingstone, Thin. Dublin: Fannin and Co. Glasgow: Stenhouse. Pp. 244.

THIS is by no means an unfavourable specimen of the class to which it belongs,—elementary chemical treatises, in which it would be very difficult to point out any error, either in fact or in inference, but which all the while leave us in some doubt concerning their *raison d'être*.

The author addresses himself especially to medical students, and hopes that what he has written may diminish the necessity for taking notes at lectures.

Rheumatism, its Nature, its Pathology, and its Successful Treatment. By T. J. MACLAGAN, M.D., Physician in Ordinary to their Royal Highnesses Prince and Princess Christian of Schleswig-Holstein. Second Edition. London: Adam and Charles Black. 8vo. 1896.

THE work before us is distinctly and purely medical. The author traces a parallelism between malaria and rheumatism, and shows that in the latter salicin plays as successful a part as does quinine in the former. He points out that the willow, from which salicin is obtained, flourishes particularly in the cold damp districts which are the home of rheumatism.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Analytische Chemie.
Vol. xxxv., Part I.

Determination of Sulphurous and Sulphuric Acids in the Products of the Combustion of Coal-gas.—M. Dennstedt and C. Ahrens.

Use of Solutions of Iodine for the Volumetric Determination of Solutions of the Alkaloids.—Dr. C. Kippenberg.—By occasion of the publication of an inquiry entitled "Contributions to the Isolation, Determination, and Chemical Diagnosis of Alkaloids and Glycosidic Substances in Judicial Cases, with especial reference to their Recognition in Putrescent Human Remains," I have made some investigations on the use of a solution of iodine obtained by dissolving free iodine in water by means of a solution of potassium iodide. It was used for the separate determination of alkaloids, and it appeared that only the free iodine of the standard liquid comes into action for the production of the insoluble periodide composed of the alkaloid. This compound is produced by the hydriodate of the alkaloid and of iodine, whilst the potassium iodide of the standard liquid remains in the first place unchanged, and is only subsequently affected by the decomposition of the water induced by the formation of the alkaloid hydriodate. The author gives an account of experiments with narcotine, strychnine, and atropine in different solutions and degrees of concentration.

Optical Determination of Alcohol and Extract in Wines.—Prof. Dr. E. Riegler.—The author makes use of Pulfrich's refractometer, which permits of a determination of the indices of refraction as far as five decimal places. The three indices required are that of the wine, of the solution of the extract, and of distilled water. The author gives a table useful in the application of his method. The constants for beer are the same as those for wine.

Method for the Determination of Uric Acid.—Prof. Dr. E. Riegler.—This method depends on the reduction of Fehling's solution to red cuprous oxide in heat. The author first determines the reductive value of uric acid with Fehling's liquid. One gram of uric acid may be regarded as a mean to represent 0.8 gram copper. This experimental result agrees very closely with the calculated quantity 0.7556 copper. He separates the uric acid from urine according to Fokker's process as ammonium urate. The reduced cuprous oxide may be weighed as such and calculated as copper, or it may be reduced to metallic copper and weighed as such. The quantity of uric acid required is found by multiplying the weight of copper found by $1000/0.8 = 1.25$.

Determination of the Purity of Oil of Bergamot.—Prof. Dr. A. Bornträger.—This paper is of little general interest.

Blackening of Vegetables Preserved in Sheet Tin Boxes.—Dr. A. Rossing.—This blackening seems to have been first observed by Beckurts (*Chemiker Zeitung*, 1889) and Beckurts and Nehring (*Apotheker Zeitung*, 1890). The dark coating observed especially on the inside of the boxes is traced to the formation of tin sulphide. It occurs only in spots where the vegetables come in direct contact with the tin. It is not confined to cans where the contents are spoiled, but also in such as contain vegetables agreeable to taste and smell. It has never been observed in cans containing beans. The tin itself sometimes becomes dissolved. Weber (*Chemiker Zeitung*, 1892) detected in pumpkins 0.054, 0.444, in cherries 0.414, in peaches 0.324, in tomatoes 0.140 stannic acid per kilo., but in peas only 0.069 and 0.043. Vegetables and fruits containing tin have been examined by Van Hamel Roos and Wefers Bettink (*Chemiker Zeitung*), who observed that 270 soldiers at Utrecht became ill after consuming canned vegetables in which 0.019 to 0.072 gram tin per kilo. was detected. The author regards the proposal of preserving vegetables and fruits in glass bottles as impracticable on a commercial scale. He approves of the suggestion of coating the cans internally with varnish. This procedure has been officially adopted by the Dutch Admiralty.

Refractive Power and Density of Dilute Solutions.—W. Hallwachs (*Ann. der Phys. und Chemie*).—There is here merely a reference to the original.

Influence of Solvents upon the Rotative Power of Organic Substances.—P. Freundler (*Ann. de Chim. et Phys.*).—The author has especially investigated the tartaric ethers. The abstractor points out that, in many cases in which strong deviations of the specific rotatory power were observed as a consequence of the action of certain solvents, the determination of the molecular weight cryoscopically or by determination of the vapour tension gave very abnormal values. The author infers that in such cases there ensues a dissociation of the rotating substance.

Use of the Critical points of Liquids as a Criterion of their Purity.—R. Pictet (*Comptes Rendus*, cxx., 43).

A Decision on the Solubility of certain Sparingly Soluble Bodies from the Electric Conductivity of their Solutions.—F. Kohlrausch and F. Rose (*Sitzungsber. der Phys. Math. Kl. der Königl. Acad. zu Berlin*).—According to these communications the experimentalist can at any time in a few seconds determine, by means of an electric current, the condition of a solution and follow the course of its formation. The contamination of the solutions and the weighing of small quantities in large capsules are ex-

cluded. The solution does not need to be separated from undissolved matter, and it may be even turbid without affecting its conductivity.

New Mercurial Air-pumps.—New constructions have been introduced by E. Lueke, of Berlin, as here figured; by G. W. A. Kahlbaum (*Annalen der Phys. und Chem.*); Schulze-Berge (*Ann. der Phys. und Chem.*), and German patent 72,329, a safety-valve for water-pump, H. Berlemont (*Bull. de la Soc. Chim. de Paris*).

On Balances and Weights.—W. H. F. Kuhlmann (*Chemiker Zeitung*) has devised a rapid balance with telescope readings. At its mean load the balance comes to an equilibrium in nine seconds. Herzberg, of the firm Paul Bunge (*Chem. Zeit.*), objects to Kuhlmann's construction. A preliminary balance, to avoid the re-adjustment of the larger weights, is proposed by Schiermann (*Chem. Zeit.*). A new system of weights has been proposed by the same author (*Chem. Zeit.*). It proceeds from 1 c.g., and has in the same series the double and quadruple weight marked 2 and 4. The octuple weight is the unit of the following series.

Adjustment and Suspensions for the Terminal Knife-Edges of Balances of Precision.—L. Armbruster.—(German patent, 72,524).

Apparatus for Fractionated Distillation.—Several new arrangements have been proposed by Marius Otto (*Bull. Soc. Chim. de Paris*); Varenne (*ibid.*); H. Wislicenus (*Berichte*); H. Schulz (*Berichte*); F. Anderlini (*Bull. Soc. Chim. de Paris*).

New Laboratory Appliances.—H. Lœmer (*Fourn. Prakt. Chemie*) describes a new stirring apparatus on the same principle as Witt's centrifugal agitator, applicable even in small flasks with narrow necks. The same author describes a water-bath with a movable ring having the construction of an iris screen.

New Apparatus.—J. Volhard (*Liebig's Annalen*).—The appliances described require the accompanying cuts.

An Arrangement for the Automatic Exhibition of a Gas Flame after a given time.—P. N. Raikow.—(From the *Chemiker Zeitung*).

Glass Cocks with a Safety Arrangement.—E. Greiner.—(A trade catalogue). The plug is held in its place by an elastic tissue.

An Extraction Apparatus.—L. Etaix.—From the *Bulletin de la Soc. Chim. de Paris*.

A Bottle with Liquid Joint.—F. Meyer (*Zeit. für Angewandte Chemie*).—The bottle is adapted for washing, drying, and absorbing gases.

A New Sulphuretted Hydrogen Apparatus.—W. Gallenkamp (*Chemiker Zeitung*).

Glass Vessels for preserving Substances sensitive to Light.—Hr. Biltz (*Pharm. Central Halle*).—The author concludes, from his experiments, that coloured glass (black or brown) does not entirely exclude the chemically active rays of light.

Luteol, a New Indicator.—W. Autenrieth (*Archiv der Pharmacie*).—Already inserted.

On Ether.—Lassar Cohn (*Liebig's Annalen*).—The author's experiments have the view of obtaining an ether absolutely free from aldehyd.

Determination of Chlorine in Bromine.—Hr. Erchentrecher (*Zeit. für Angewandte Chemie*).—The author weighs off 20.6 grms. of sodium bromide free from chloride, and dissolves so as to make up 1 litre; 25 c.c. of this solution are added in an Erlenmeyer flask to 6 grms. of the bromide in question, and evaporated. The solution is boiled up, rinsed into a capsule, evaporated to dryness, ignited gently, and weighed. The proportion of chlorine can be found by means of a table.

On Technically Pure Starch Sugar, and on Wine obtained with its Use.—Prof. Dr. R. Fresenius.—A study referring to the German laws on the use of improper materials in the manufacture of foods and beverages. The author contends that starch sugars and their products, though not technically pure, are not objectionable on hygienic grounds.

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Poggendorff's Annalen der Physik u. Chemie.
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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1912.

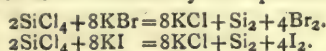
NOTES ON THE REPLACEMENT OF CHLORINE IN THE CHLORIDES OF THE NON-METALS AND METALLOIDS BY BROMINE AND IODINE.

By H. LLOYD SNAPE, D.Sc., Ph.D.

R. Brix (*Liebig's Annalen*, 1884, cxxv., 146), B. Koehnlein (*Ibid.*, cxxv., 171), and H. Spindler (*Ibid.*, 1885, ccxxxi., 257) have shown that the elements chlorine, bromine, and iodine replace one another in many organic haloid compounds, when these are heated with metallic chlorides, bromides, and iodides. The object of the experiments detailed below was to determine whether the chlorides of the non-metals would not undergo a similar decomposition when heated with potassium bromide and potassium iodide respectively.

G. Gustavson (*Berichte*, 1874, vii., 128; *J. d. Russ. Chem. Gesellschaft*, 1881 [1], 288) found that carbon tetrachloride was converted, by aluminium iodide in carbon disulphide solution, into carbon tetriodide, and, in the paper to which reference has been made above, Spindler showed that carbon tetrachloride may be converted into the corresponding iodide by treatment with potassium iodide.

G. Rauter (*Liebig's Annalen*, 1892, cclxx., 246) investigated the behaviour of silicon tetrachloride towards a large number of mineral compounds of varied types, and found, *inter alia*, that this chloride was but little attacked by potassium bromide and potassium iodide. The chemical changes which did take place to a slight extent, he considered to be indicated by the equations—



E. Bamberger and J. Philipp (*Berichte*, 1881, xiv., 2643) described the formation of arsenious iodide by the addition of a strong aqueous solution of potassium iodide to a hydrochloric acid solution of arsenious oxide.

I anticipated that the strongly basic element potassium would readily remove chlorine from its comparatively unstable combinations with the non-metals, and that the latter when liberated would probably unite with the bromine or iodine simultaneously set free.

Owing to the readiness with which most of the non-metallic haloids are attacked by water, it was obviously necessary, in the majority of cases, to work with absolutely dry materials and out of contact with air; hence my experiments were carried out in sealed tubes. Moreover, as the non-metallic bromides and iodides which I hoped to obtain are even when dry in many cases decomposed by heat, but at temperatures not always stated in the literature, it would evidently be advantageous to have the contents of the tubes under observation, so that in the event of such decomposition the liberation of bromine or iodine would at once be recognised, and the temperature might be reduced; hence some of the sealed tubes were heated in a deep glass bath containing paraffin. As, should the undecomposed chloride remain behind with the bromide or iodide of the non-metal formed, the separation would be difficult, I employed in all instances an excess of the metallic salt.

Proceeding in this way I found that, by means of potassium bromide, sulphur monochloride and arsenic trichloride were partially converted into their respective bromides, but, on the other hand, no similar conversion could be effected by the action of the first-named com-

pound upon carbon tetrachloride and phosphorus trichloride. Carbon tetrachloride behaved in an analogous manner to silicon tetrachloride as described by Rauter; phosphorus trichloride was apparently unchanged.

I also further examined the behaviour of the same potassium salt towards the trichloride of the metalloidal element antimony.

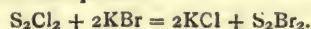
R. W. Atkinson (*Journ. Chem. Soc., Trans.*, 1883, xliii., 283) had already shown that on mixing strong solutions of antimony trichloride and potassium bromide, or of antimony tribromide and potassium chloride, the same compound ($\text{K}_3\text{SbBr}_3\text{Cl}_3$) was obtained. This was, however, decomposed by heat-yielding vapours in equivalent proportions of antimony trichloride and tribromide. Hence I expected that on passing the vapour of antimony trichloride over a long layer of potassium bromide, heated to a sufficiently high temperature to decompose the double salt, most, if not all, of the antimony trichloride would be converted into antimony tribromide. This change actually occurred.

The results of the similar experiments conducted with potassium iodide are as follows:—Phosphorus trichloride, arsenic trichloride (Bamberger and Philipp had used hydrochloric acid solution of arsenious oxide), and antimony chloride, were readily converted into their respective iodides; carbon tetrachloride was only in part attacked, and yielded only free carbon and iodine, again behaving analogously to silicon tetrachloride; sulphur monochloride was much more completely decomposed, and also yielded no definite iodide, but only the elements sulphur and iodine.

For the convenience of comparison I repeated the method of Guthrie (*Journ. Chem. Soc., Trans.*, 1862, xiv., 57) for the preparation of sulphur moniodide, and I have made a few notes on this which will be found below.

Sulphur Monochloride and Potassium Bromide.

5.4 grms. of sulphur monochloride of b.p. $136^\circ-8^\circ$ were heated with 12.7 grms. of dry potassium bromide (only 9.5 grms. of the latter theoretically required for mutual decomposition), first for one hour at 100°C . At this temperature there was no apparent change. The temperature was then maintained for two hours at 180° to 190° , and then for over seven hours at 200° to 220° . The tube stood for some days before being opened. The contents, which were of a pasty consistence, were extracted with carbon disulphide, and the liquid extract was subjected to fractional distillation. Bromine began to come over at 60° , and the temperature rose steadily up to 230° , when a black mass of sulphur remained behind. Between 160° and 220° there passed over 5.4 grms. of a dark red liquid, which decomposed, on re-distillation, some bromine first passing over and some sulphur remaining behind. This corresponds to the unstable compound S_2Br_2 , which Pattison Muir (*Journ. Chem. Soc., Trans.*, 1875, xxviii., 845) held was formed by the direct union of sulphur and bromine. Had this been formed in the present case, reaction must have taken place in accordance with the equation—



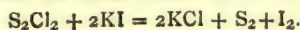
Theoretically, 9 grms. of sulphur monobromide should thus have been produced, had the reaction been quantitative; but doubtless some portion of this compound, if formed at all, underwent dissociation during the first distillation.

Sulphur Monochloride and Potassium Iodide.

3.8 grms. of sulphur monochloride were treated with 12 grms. of perfectly dried potassium iodide (one-third more than the theoretical quantity of the latter). Some reaction took place as soon as the substances were mixed, a violet-red colour being acquired. In order to render the reaction more complete, the whole was heated for rather more than two hours at 60° to 80° . The cooled residue was reddish brown in colour, compact, and very hard, and

contained a large number of small lustrous crystals. The whole mass was repeatedly extracted with carbon disulphide, deep violet solutions being obtained. The entire extract was then distilled to remove excess of solvent, and the concentrated solution cooled. The first crystals, which were dark in colour and not unlike iodine, were redissolved in carbon disulphide, and by fractional re-crystallisation portions A, B, and C were successively obtained. From the original mother-liquor two additional lots of crystals, D and E, were separated. The crystals E, which separated last from the original solution, consisted of almost pure sulphur, and were yellow in colour and transparent. The other crystals were all very dark in colour, and though C and D consisted of well-formed octahedra, and appeared at first sight to be homogeneous, they proved to be constituted of mere mixtures of sulphur and iodine. On merely standing in air at ordinary temperature, they lost iodine, and free sulphur remained behind. This afforded a ready means of determining the percentages of sulphur they respectively contained, though for analytical purposes the decomposition was facilitated by heating on the top of a steam-oven. Portions A, B, C, and D were thus found to contain only 0.46, 0.24, 1.2, and 1.14 per cent of sulphur respectively. A determination of sulphur in another portion of the crystals D was made by Carius's method, and gave 1.4 per cent.

The above results are most easily explicable on the hypothesis that the main reaction is—



From a solution of sulphur and iodine in carbon disulphide, iodine being the less soluble, the first crystals to separate out would naturally consist mainly of this element, the later products of crystallisation containing more sulphur, and finally pure sulphur would be obtained. This would accord with the actual experimental results.

The above result led me to investigate the reaction by which F. Guthrie (*Journ. Chem. Soc., Trans.*, 1862, xiv., 57) first prepared (?) sulphur moniodide. His method consisted simply in mixing sulphur monochloride and ethyl iodide in equivalent proportions, and removing the ethyl chloride formed by applying gentle heat. The only evidence offered in support of the view that sulphur moniodide had been produced was an analysis of the residue; but the ethyl group having combined with chlorine, this residue would necessarily contain sulphur and iodine in equi-atomic proportions, whether combined or uncombined: $2\text{C}_2\text{H}_5\text{I} + \text{S}_2\text{Cl}_2 = 2\text{C}_2\text{H}_5\text{Cl} + \text{S}_2 + \text{I}_2$.

Sulphur Monochloride and Ethyl Iodide.

2.3 grms. of sulphur monochloride and 6.1 grms. of ethyl iodide were introduced into a sealed tube, which was then exposed to the sun's rays for several days, but was not subjected to any artificial heat. The liquid gradually deepened in colour, and on the second day crystals separated. After an interval in all of five days, the drawn-out end of the tube was broken and attached to a calcium chloride tube, and the ethyl chloride was allowed to spontaneously evaporate. Any residual ethyl chloride was removed by connecting the tube to a filter-pump, and warming the contents by the hand. The dry crystalline mass which remained smelt strongly of onions (probably due to a trace of some compound of a mercaptan nature). Though the crystals appeared at first sight to be homogeneous and dark, an examination under a microscope showed that they consisted of a mixture of light yellow transparent crystals of sulphur and black opaque crystals of iodine, and, on treating a small quantity on a watch-glass with ether, only the former remained unchanged in the original rhombic crystals. 0.3894 gm., after the iodine had been removed by standing on the top of a water-oven, and later in a desiccator, yielded a residue of 0.0785 gm., equivalent to 20.16 per cent of sulphur. The percentage of sulphur required for the formula S_2I_2 is 20.13. Guthrie obtained, by fusing his crystals with

potassium nitrate and sodium carbonate, 20.28 per cent. Such analyses, however, do not afford any proof of the existence of the compound S_2I_2 . As stated above, whether chemical union has occurred or not, equivalent proportions of sulphur and iodine necessarily constitute the residue after the expulsion of ethyl chloride.

Carbon Tetrachloride and Potassium Bromide.

4 grms. of carbon tetrachloride of b.p. 76.5° were heated with the equivalent quantity of potassium bromide in a sealed tube, for seven hours at 200° . After cooling, the bulk of the solid was seen to have acquired a pale yellow colour; small dark-coloured particles were also visible in the mass. The whole was extracted with ether, which took out bromine, and on evaporation left only a mere trace of a dark red substance. Hence carbon tetrabromide was not formed. The residue was grey, and contained, in addition to the white potassium salts, a small quantity of dark brown carbonaceous substance insoluble in water.

Carbon Tetrachloride and Potassium Iodide.

2.7 grms. of carbon tetrachloride were similarly treated with an equivalent quantity of potassium iodide, for three and a half hours at 200° . During this treatment free iodine was evidently evolved, and the reddish brown mass obtained on cooling contained crystals of iodine. The whole was extracted in a Soxhlet's apparatus by means of ether, and the ethereal extract was evaporated. Only a very small quantity of a dark-coloured substance was obtained, and this gave off iodine on being heated, and left a black residue, probably consisting of carbon.

The residue, which was left after complete exhaustion with ether, was still light brown in colour, and, on addition of water to dissolve the potassium salts, there was a small insoluble residue, evidently consisting of a carbon compound or amorphous carbon.

Phosphorus Trichloride and Potassium Bromide.

4.6 grms. of phosphorus trichloride of b.p. 76° to 78° were heated with a slight excess of potassium bromide, for eight hours at 200° to 220° . After the sealed tube had stood for a few days at the ordinary temperature, it was opened, and the contents, consisting of a moist greyish mass, were exhausted by chloroform. The chloroform extract was then distilled, when the greater part passed over at 61° ; then the temperature rose to 63° – 64° , and finally a very small fraction passed over at 65° . Thus the temperature at no time reached even the boiling-point of phosphorus trichloride, much less that of the tribromide (175°). The distillates fumed strongly in contact with air, and evidently contained unaltered trichloride which had passed over with the chloroform.

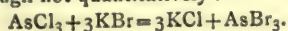
Phosphorus Trichloride and Potassium Iodide.

As soon as phosphorus trichloride was mixed with potassium iodide there was a slight evolution of heat, and the mass acquired an orange colour. To render the reaction more complete, the whole was heated for two and a half hours at about 200° . The phosphorus triiodide, which was at once recognisable after cooling the tube, was extracted by carbon disulphide, and separated from this solution, after evaporation *in vacuo*, in crystals which possessed the characteristic red colour and melted at 55° . This reaction was in accordance with the equation $\text{PCl}_3 + 3\text{KI} = 3\text{KCl} + \text{PI}_3$.

Arsenic Trichloride and Potassium Bromide.

Five grms. of arsenic trichloride (b.p. 131.5° – 132.5°) were heated with excess of potassium bromide for more than ten hours at from 180° to 220° . The cooled tube-contents, which had a slight brown colour, were exhausted with chloroform, and the extract was then fractionally distilled. The last fraction passed over between 130° and 90° , and weighed 3.8 grms. This was surrounded by a

freezing mixture, when the whole became apparently one solid mass. As the temperature was allowed to rise, a part became fluid again, so that at 0° only about two-thirds of the original mass of crystals remained, at 2° only about one-third, and at 11° the whole had become fluid. The melting-point, like the boiling-point of the bromide, had evidently been reduced by the presence of unaltered chloride. As the quantity was too small for further fractionation, the crystals which remained, as described above, at 2° were analysed by dissolving in excess of sodium-hydrogen carbonate solution and titrating with standardised iodine solution in presence of starch. The crystals were found to contain 25.92 per cent As, which indicated that the arsenic bromide still contained 12 per cent of arsenic chloride; the calculated percentage of arsenic in the bromide and chloride being 23.81 and 41.32 respectively. The following reaction had thus occurred, though not quantitatively:—



Arsenic Trichloride and Potassium Iodide.

Bamberger and Philipp having already shown that arsenic iodide is formed on the addition of an aqueous solution of potassium iodide to a solution of arsenious anhydride in hydrochloric acid, it was practically certain that arsenic chloride and potassium iodide would readily attack one another in the dry state, but to make this series of reactions complete, the actual experiment was tried. On mixing these two compounds at the ordinary temperature partial reaction occurred, and heat was evolved. After heating the mixture in a sealed tube to about 240° and then cooling, the characteristic highly lustrous red tables were seen to have been formed throughout the mass. They were readily re-crystallised from ether or benzene; separating from benzene in especially fine crystals.

Antimony Trichloride and Potassium Bromide.

After heating these two substances, both being in dry condition, with one another, no antimony tribromide could be extracted by solvents. Hence in all probability the same compound ($\text{SbK}_2\text{Cl}_3\text{Br}_3$) had been formed, as Atkinson obtained on bringing the same two reagents together in presence of water. As Atkinson states this compound decomposes on heating, with evolution of equivalent quantities of antimony trichloride and antimony tribromide, the conversion of the former into the latter might be effected by passing it over a long layer of heated potassium bromide.

A fractional distillation flask, containing 10 grms. of crystallised antimony trichloride, was connected with a long hard glass tube lying in a combustion furnace, and along which 20 grms. of potassium bromide were evenly spread in a thin layer. The further end of the combustion-tube was constricted and bent downwards into another fractional distillation flask. The potassium bromide having first been heated, and the pressure greatly reduced throughout the apparatus by means of a water air pump, the antimony trichloride was driven over slowly. The distillate condensed in the further flask to a crystalline mass. This was re-distilled to free from any potassium or oxy-salts; 8.3 grms. passing over between 220° and 250°; this last was again fractionated, when about one-half passed over between 230° and 240°, and the remainder between 240° and 250°. The last few drops were separately collected, and were found by titration with standardised iodine solution, after dissolving with the aid of tartaric acid and addition of excess of sodium-hydrogen carbonate, to contain 38.41 per cent antimony. This would indicate (as SbBr_3 and SbCl_3 contain respectively 33.7 and 53.39 per cent Sb) that this portion contained 76.1 per cent of antimony tribromide. The fraction boiling between 230° and 240° yielding, on the other hand, 45.19 per cent Sb, equivalent to only 41.6 per cent of antimony tribromide in this mixture.

Antimony Trichloride and Potassium Iodide.

These two compounds were heated together for two to three hours at about 200°, when complete mutual decomposition readily occurred. $\text{SbCl}_3 + 3\text{KI} = 3\text{KCl} + \text{SbI}_3$. The antimony iodide was readily extracted by carbon disulphide, and was obtained from this solution in characteristic highly lustrous red crystals, which melted at 165°.

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STUDY ON CAST VANADIUM AND VANADIUM CARBIDE.

By HENRI MOISSAN.

WE have formerly indicated that vanadic acid can be reduced by means of coke in the electric furnace, yielding cast vanadium, which contains from 17 to 25 per cent of carbon. Thanks to the kindness of M. Heeren, who has placed at our disposal a considerable quantity of ash derived from a vanadiferous coal, we have been able to continue and extend these researches.

Treatment of the Vanadiferous Ash.—The ashes mixed with fragments of coal, as sent me, contained about 8 to 10 per cent of vanadic acid. They were roasted in the muffle so as to destroy all the carbonaceous portions, when their proportion of vanadic acid was increased to 38 per cent.

Five hundred grms. of ash were placed in a 2-litre flask on the sand-bath, and attacked with nitric acid, to which was added, at considerable intervals, a small quantity of hydrochloric acid. The soluble matter was taken up in water, and the insoluble residue was washed. After filtration through cloth, all the liquids were mixed together and evaporated to dryness. The residue was dissolved in ammonia diluted to one-tenth, yielding a first solution of ammonium vanadate, which was then precipitated with nitric acid, to furnish crude vanadic acid.

The insoluble residue was exhausted with ammonia diluted to one tenth, yielding a further quantity of vanadate which was treated in the same manner with nitric acid.

The crude acid thus obtained was purified by L'Hôte's method (*Ann. de Chim. et de Phys.*, Series 6, xxii., 407, 1891). The vanadium is transformed into vanadyl chloride, which latter is decomposed with water.

The vanadyl chloride was obtained at 250°, and the redification was effected by fractions of 1500 grms. by means of a bulb-apparatus. Vanadyl chloride distils at +126.5°, the figure indicated by L'Hôte.

By decomposition with water we obtain pure vanadic acid, which is then dried with care.

Preparation of Cast Vanadium.—Vanadic acid was mixed with the charcoal of sugar, finely pulverised, in the following proportions:—

Vanadic anhydride	..	..	182 grms.
Sugar charcoal	..	..	60. „

Of this mixture 300 grms. were heated in the electric furnace with a current of 900 ampères and 50 volts. The duration of the experiment is five minutes. In this manner we obtained a highly carburated vanadium, which on analysis gave the following figures:—

	1.	2.	3.	4.	5.
Carbon ..	10.5	13.8	11.6	16.2	15.9

In another series of experiments we employed:—Vanadic anhydride, 100; charcoal, 20; and we obtained castings containing, per cent, 9.9, 9.2, 9.83.

All these experiments have been made in tubes of coke. It is necessary to employ an intense current of very short duration, because the anhydride easily fuses and completely moistens the coke of the tube. In this case the carburation is very rapid.

When we attempted to refine cast vanadium by means of vanadic anhydride all our experiments have proved fruitless, by reason of this easy liquefaction of vanadic acid. The beautiful researches of Prof. Roscoe have, moreover, shown that the preparation of vanadium is one of the most difficult problems of mineral chemistry.

The powerful affinity of vanadium for nitrogen further augments these difficulties. It is useful to reach a very high temperature to effect the destruction of the nitride.

On heating pure vanadic acid for two minutes only in a coke tube, with a current of 1000 ampères and 60 volts, and taking care to keep up a constant current of hydrogen in the coke tube, we succeeded in obtaining cast vanadium not containing more than 5·3 to 4·4 of carbon.

Another specimen, heated for three minutes, gave us 7·42 of carbon.

Properties of Cast Vanadium.—Cast vanadium containing 5 per cent of carbon has a white colour, a brilliant fracture, metallic, not oxidisable in the air, and a sp. gr. of 5·8 at +20°.

Prof. Roscoe found 5·5 for vanadium containing traces of oxygen, and 1·3 per cent of hydrogen.

This cast metal burns with incandescence in oxygen at a red heat. Chlorine attacks it at a dark red heat without incandescence. With nitrogen it combines readily. In a general manner this cast metal is attacked by acids more readily than the definite carbide of which we have to speak. Hydrochloric acid attacks it neither in cold nor in heat, whilst sulphuric acid, concentrated and boiling, attacks it very slowly. Its other properties are comparable to those of Prof. Roscoe's vanadium.

Preparation of Vanadium Carbide.—If we heat, in the electric furnace, vanadium anhydride mixed with sugar and charcoal in a tube of coke for nine to ten minutes (900 ampères and 50 volts), we obtain a regulus formed of a definite vanadium carbide, which gives up a small quantity of graphite at the moment of its solidification.

Properties of Vanadium Carbide.—CVa is volatile when strongly heated in the electric furnace. Its melting-point is a little higher than that of molybdenum. In the liquid state it has a metallic aspect. Its sp. gr. is 5·36. It scratches quartz easily, and occurs in beautiful well-defined crystals.

Chlorine attacks it with incandescence above 500°, yielding a liquid chloride easily volatile. In oxygen it burns at a dark red heat with a lively incandescence. It does not combine with sulphur at the melting-heat of glass. Nitrogen and ammonia attack it at a red heat with formation of nitride. At dark redness it does not react with gaseous hydrochloric acid, watery vapour, and hydrogen sulphide.

Hydrochloric and sulphuric acids do not attack it, but it reacts with nitric acid in the cold. Melting oxidising agents—i. e., potassium nitrate and chlorate—decompose it at a dark red heat. With the chlorate there ensues a brisk incandescence.

Analysis.—Vanadium carbide yielded the following figures:—

	1.	2.	Theoretical CVa.
Carbon	18·39	18·42	18·98
Vanadium	81·26	80·79	81·01

Alloys of Vanadium.—Notwithstanding its high point of fusion, vanadium readily yields alloys, some of which we have studied.

If we heat, in the electric furnace, for three minutes, a mixture of oxide of iron, vanadium anhydride, and sugar charcoal, so as to yield an alloy containing 20 per cent of vanadium (900 ampères and 50 volts), we obtain a homogeneous ingot of a greyish white with a crystalline fracture, and capable of being filed. It contains—

Iron	72·96
Vanadium	18·16
Carbon	8·35

A mixture of vanadium anhydride, of copper oxide, and of charcoal,—a mixture calculated to yield an alloy containing 5 per cent of vanadium,—yielded, in the electric furnace, a well-fused regulus of a bronze colour, very malleable, capable of being filed with ease, and harder than copper. It contained:—Copper, 96·52; vanadium, 3·38.

We can prepare an alloy of aluminium and vanadium by keeping aluminium in fusion at the bottom of an earthen crucible, and projecting upon the surface of the metal a mixture of vanadic acid and aluminium filings. There ensues a brisk incandescence, and on stirring up the mass we obtain an alloy of aluminium and vanadium very malleable, rather soft, and which if filed clogs the tool. It contains 2·5 per cent of vanadium.

In another experiment we heated, in the electric furnace, a mixture of reduced silver with quantities of vanadic anhydride and of charcoal, calculated for an alloy of 10 per cent. The duration of the heating was three minutes, and the current 900 ampères and 50 volts. We thus obtained a metallic ingot formed of two superimposed layers; on the one part vanadium without a trace of silver, and beneath silver with its fine white colour, which when dissolved gave no reaction of vanadium. These two substances, therefore, have no action upon each other.

Conclusions.—On reducing vanadic acid with charcoal in the electric furnace, we can obtain easily and plentifully a cast vanadium containing 4 to 5 per cent of carbon. If the heating is more prolonged we always obtain a new carbide, definite and crystalline, of the formula CV. This compound does not act upon water at ordinary temperatures, and is more stable in presence of acids than in cast vanadium.

At the temperature of the electric furnace, vanadium combines with iron, copper, and aluminium, but it forms no alloy with silver.

From the totality of these properties vanadium approximates more to the non-metals than to the metals. Its carbide, approaches the titanium and zirconium carbides which have the same formula.—*Comptes Rendus*, cxxii., p. 1297.

ACTION OF MERCURY SALTS ON ALUMINIUM.

By PERCY A. E. RICHARDS, F.I.C.

Now that aluminium is so extensively used for various instruments, the following reaction that recently came under my notice may perhaps be of general interest:—

A few days ago I was using an aluminium spatula to remove some solid substances from bottles to test-tubes, and having wiped it and laid it on the table, I was surprised to notice that in a couple of minutes the end had become covered with a coating of white powder. I rinsed it thoroughly under water, wiped it dry, and again laid it down. In a very few minutes, however, it was covered as before, and on examining the coating carefully I found it had the appearance of a brush-like "growth" consisting of white filaments standing upright on the flat surface. Whilst watching them they increased visibly, and resembled somewhat the white "hyphae" of *Mucor mucedo*.

A few experiments with the different powders used showed that mercuric iodide was the initial cause of the phenomenon, as this substance produced the same effect when placed on a strip of aluminium. I next tried the action of other solid mercury salts on pieces of this metal under similar conditions, and in each case found that the same "growth" followed. In fact, if the salt was left in contact with the metal for only a minute, and the latter at once wiped or washed, in a short time the brush-like masses of filaments appeared and steadily increased. A

minute globule of mercury also sufficed to start the action. It seems to me that this result is brought about by the mercury first forming an amalgam with the aluminium, and this, reacting at once on the moisture present in the air or on the surface of the metal, forms alumina, at the same time liberating the mercury, which once more forms amalgam. Repeated washing appears to check the action very slightly if once the mercury gets a firm grip on the aluminium.

An approximate determination of the amount of decomposition brought about in a given time was made as follows:—A weighed strip of aluminium was dusted over on both sides with powdered mercuric chloride, and after remaining in contact for a couple of minutes, the latter was washed off and the strip roughly dried. After an hour's interval the metal was again thoroughly washed and dried, and then weighed, when the loss of aluminium had amounted to a little over 8 per cent of the whole. Qualitative analysis of the white filaments showed them to consist, as was supposed, of alumina.

In short, these results show that the greatest care should be taken to prevent any apparatus, &c., of aluminium being brought into contact with mercury in any shape or form.

I have no doubt that other chemists have had similar experiences, and indeed results such as these are only what might be expected considering the powerful action of aluminium amalgam as a reducing agent.

ON THE PERIODIC CLASSIFICATION OF THE ELEMENTS.

By Dr. WYROUBOFF.

SINCE the evening when the periodic classification of the elements was first laid before the Chemical Society by Mr. Newlands, it has been singularly exempt from criticism—unfair, or even severe. Hence we need not be surprised at the discourse of Dr. Wyruboff. If, remarks Dr. Wyruboff, the classification of Prof. Mendeleeff had remained what it was at its outset, *i.e.*, a very interesting and highly ingenious table of the analogies and the dissimilarities of the simple bodies, I should never have entertained the idea of discussing it before you.

But M. Mendeleeff has aimed at producing something more and better than a mere *catalogue raisonné* of the elements. He converted his classification into the periodic system. It was a philosophic view, borrowing arguments from the kindred sciences, and imposing itself on us by its universality. He formulated, as the fundamental law of the physico-chemical sciences, the dictum that "all the properties of bodies are periodic functions of their atomic weights."

It would seem that, in view of a question so distinctly put, the first duty of the *savant* must be to intervene, as has been done with particular laws, to check and verify them down to the utmost details. This has not been done—not even dreamt of—and we find, not merely in special researches, but even in works of elementary instruction, the periodic law accepted as a reality beyond all disputes. Periodicity being the general and infallible law, the table of Mendeleeff could not err. In works otherwise excellent I have met with the assertion that "no chemical argument could avail against the periodic law."

On reaching this point of its development, the conception of Prof. Mendeleeff becomes essentially injurious. Under pretext of a law which has still to be demonstrated, it forbids us to throw light upon pure matters of observation, and forces us to remain in a vicious circle from which there is no escape. I think that it is time to show clearly that there is nothing which merits the name of *law* or *system*.

I shall consider here merely properties of a purely che-

mical order, the only ones which chemists have to take into account. Let us take on the one part the atomic weight, and on the other the valence. I say that between these two facts, both constituting chemical attributes absolutely irreducible, we do not see any kind of necessary connexion. No known law permits us to conclude that between these two orders of things, absolutely distinct, there is any relation which we may establish without leaving the proper sphere of chemistry. The "periodic law," which claims to establish such a relation, gives us no theoretic antecedent. This by no means implies that it is necessarily false; it signifies merely that it is an empirical law, and as such it is bound to furnish multiple proofs of validity. Among these proofs, without which no empirical law even can acquire the "freedom of the city," it must be demonstrably free from exception. As Mendeleeff puts it:—"The laws of Nature admit no exception; therefore, the periodic law must be considered as a law of Nature definitely established, which must be accepted or rejected as a whole" (*"Elements de Chimie,"* 1889, 5th Russian edition, p. 465).

A surprising exception is presented by the atomic weight of tellurium. Professor Brauner, who has made a speciality of the art of causing reluctant elements to enter into the classification of Mendeleeff, opens his memoir by laying before us two alternatives: we must either reject the "periodic law," or reject the figure 128 which all authorities have found for the atomic weight of tellurium. But, he continues, as the periodic law cannot be rejected, since it is the truth itself, the value 128 must be inaccurate.

He has therefore submitted tellurium to all the tortures which a substance can undergo. He has melted it, sublimed it, oxidised it, hydrogenised it, dissolved it, and precipitated it, and finally arrived at the result which everybody had reached before him, that the atomic weight varies between the wide limits of 125 and 129.

Hence he concludes that we have here a complex body composed of two elements of very different atomic weights. What are these weights, and what are the distinctive properties of tellurium α and tellurium β he does not tell us, for he has not been able to separate them. Still, he takes the number 125 as representing true tellurium, and Prof. Mendeleeff introduces this number in his table, though it has not yet been confirmed by any one.

Prof. Mendeleeff admits for the three cerite metals $La=138$, $Ce=140$, and $Di=192$. He required this succession, since cerium yielding a higher oxide could not be placed upon the ascending branch of the curve before lanthanum. But Marignac, Bunsen, Jögel, Rammelsberg, and Wolf have found $Ce=138$, with deviations not exceeding one or two units of the first decimal. Prof. Brauner alone has obtained 140 by the calcination of the sulphate, a process absolutely defective, as Schützenberger has recently pointed out. As for lanthanum, the majority of recent determinations lead to a figure very near 138.5. Mendeleeff, to give more symmetry to his curve, selected that which presents the lowest figure. As for didymium, it is especially embarrassing for the periodic classification. In 1886 it was split up by Auer von Welsbach into neodymium ($Nd=141$) and praseodymium ($Pr=143.6$). Now, this latter gives on calcination an oxide higher than R_2O_3 , whence neodymium ought to be placed on the same horizontal line as lanthanum. This part of the curve would then become quite irregular, whence Mendeleeff retains in his table of 1889 the old didymium, contenting himself with asserting that the two new metals ought not to be simple bodies, and that there is no occasion to occupy ourselves with them.

The arbitrary selection of oxides and of atomic weights is the gravest critique which we are justified in addressing to Prof. Mendeleeff.

The objections to the "periodic law" urged by Dr. Wyruboff certainly merit a very careful consideration.—*Les Actualit es Chimiques.*

THE USE OF PHENOLPHTHALEIN IN ILLUSTRATING THE DISSOCIATING ACTION OF WATER.

By HARRY C. JONES and CHARLES R. ALLEN.

THE fact that an alcoholic solution of phenolphthalein is not coloured red by ammonia or triethylamine, but is so coloured by potassium, sodium, or barium hydroxide, was observed by Menshutkin (*Ber. d. Chem. Ges.*, xvi., 315). He stated that if phenolphthalein is added to alcohol, it does not show an alkaline reaction on the addition of triethylamine or ammonia, and he concluded that the alkalinity of the triethylamine had disappeared, alcohol decomposing the compound of phenolphthalein with triethylamine, even when the latter is present in a large excess.

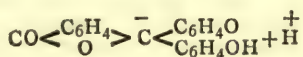
Without knowing of this work of Menshutkin, we observed facts of the same kind in connection with an investigation which is being carried out in this laboratory by Mr. Mackay. Not only an alcoholic solution of ammonia did not show an alkaline reaction with phenolphthalein, but when a few drops of a water solution of ammonia were added to several c.c. of alcohol, this solution also failed to give an alkaline reaction with alcoholic phenolphthalein. If, however, a considerable volume of water was added to this solution the red colour appeared.

When potassium or sodium hydroxide was substituted for ammonia the red colour appeared at once, without the addition of water, as stated by Menshutkin. There is thus a marked difference between the action of sodium and potassium hydroxides on the one hand, and that of ammonium hydroxide on the other.

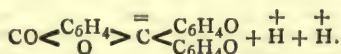
It would be difficult to interpret these facts without the aid of the dissociation theory, unless we were content simply to say that potassium and sodium hydroxides are stronger bases than ammonium hydroxide, which really explains nothing. This difficulty becomes the more apparent in that Menshutkin was compelled to seek an explanation in the decomposition of the compound of phenolphthalein with triethylamine by alcohol. In the light of the dissociation theory, however, the facts become intelligible.

In a solution prepared by adding a few drops of aqueous ammonia to several c.c. of alcohol, little or no dissociation of the ammonium hydroxide is effected. The addition of water to this solution dissociates the base, the degree of dissociation depending on the amount of water, with respect to alcohol present. The presence of the ions

NH_4^+ and OH^- , into which the ammonium hydroxide dissociates, will cause the phenolphthalein to dissociate into:—



or—



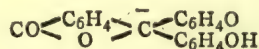
The complex anion is coloured and gives the characteristic colour to the solution in which it is present as an ion. When this coloured anion is combined with the colourless cation, hydrogen, to form a molecule, the solution of these molecules is nearly colourless. When the dissociation of the phenolphthalein indicated above is

effected, its cation H^+ would combine with the anion OH^- from the ammonium hydroxide, forming water, since these ions cannot, to any appreciable extent, remain uncombined in the presence of each other.

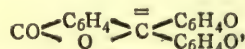
It may be, however, that the actual course of the reaction is slightly different from that above described, in that the ammonium may first combine with the phenolphthalein in the alcoholic solution. The addition of water

would then dissociate this compound, liberating the coloured anion referred to above.*

In either case the cause of the colour is the presence of the anion,—



or—



and the dissociation of the compound yielding this coloured anion is effected by the water which is present. The dissociation theory furnishes this explanation. It remains to determine whether the explanation is true. If it is, then a solution formed by adding a little aqueous ammonia to a considerable volume of alcohol should show little or no dissociation, and the amount of dissociation should increase with the addition of water. Solutions of potassium or sodium hydroxide in mixtures of alcohol and water should be more dissociated than corresponding solutions of ammonium hydroxide. Indeed, a solution of sodium or potassium hydroxide in alcohol alone should manifest some dissociation, since, as stated above, it gives the colour reaction with phenolphthalein.

All of these points can be tested experimentally by the conductivity method. We have carried out such measurements as seemed desirable, and give the results in the following tables. Table I. contains the results for ammonium hydroxide. The conductivity of a known volume of a standard solution of aqueous ammonia was at first determined. A measured volume of this solution was then removed, an equal volume of absolute alcohol added, and the conductivity again determined. This process was repeated until nearly all of the water had been removed, the solvent being nearly pure alcohol.

The values under v are the number of litres which would contain a grm.-molecular weight of the ammonium hydroxide at the particular dilution of the solution used. The column μv gives the molecular conductivities at the volume v and at 25°C . That portion of the solution which was withdrawn in each case after the conductivity reading had been made, was placed in a Nessler tube, treated with some phenolphthalein, and the strength of the red colour observed approximately. These observations are recorded in the column headed "Colour." No correction is introduced in the results for the conductivity of the water used, since this was tested, and for water which had been re-distilled from acid and alkaline permanganate, was so slight that it is quite negligible.

The corresponding measurements for potassium hydroxide are given in Table II.

TABLE I.

v .	μv .	Parts water.	Parts alcohol.	Colour.
11	4.8	100	0	Strong.
22	2.2	50	50	Slight.
44	1.0	25	75	None, or trace.
88	1.1	12.5	87.5	None.

TABLE II.

v .	μv .	Parts water.	Parts alcohol.	Colour.
8.8	21.4	100	0	Strong.
17.6	77	50	50	"
35.2	26	25	75	"
70.4	20	12.5	87.5	"

The conductivity of a standardised solution of potassium hydroxide in pure alcohol alone, was determined with the following results:—

* Long (*American Chemical Journal*, xi., 84) has shown that when strong aqueous ammonia is allowed to set on phenolphthalein for a considerable time, phenoldimidophthalein, a colourless substance is apparently formed. If this compound should be formed to some extent in the alcoholic solutions under discussion, its presence would not affect the colour reactions of the solutions in question, since it is soluble even in alkalis without colour.

v.	µv.	Colour.
8	15	Strong.

The appearance of the red colour when water is gradually added to an alcoholic solution of phenolphthalein containing ammonia is not sudden. As the results show, it requires the addition of a considerable volume of water before any trace of red can be detected, then a delicate pink colour appears, gradually shading off into red, in the presence of more and more water. This would also be expected, if the colour is a function of the dissociation, since the latter increases gradually with the increase in the water present. The results thus appear to confirm at all points the deductions from the dissociation theory.

This experiment furnishes a very satisfactory lecture demonstration of the dissociating action of water. A few drops of an alcoholic solution of phenolphthalein are placed in a glass cylinder and diluted to, say, 50 c.c., by the addition of alcohol. A few drops of an aqueous solution of ammonia are then added. A red colour may appear where the aqueous ammonia first comes in contact with the alcoholic phenolphthalein, but this will disappear instantly on shaking the cylinder, leaving the solution with a yellowish tint, possibly due to the formation of the ammonium salt of phenolphthalein. Water is then gradually added to the cylinder, when the red colour appears, first faint, then stronger as the amount of water increases. When the red colour has become intense, add a considerable volume of alcohol and the entire colour will disappear, leaving a solution which is slightly yellow. The experiment serves then not only to illustrate the dissociating action of water, but also the driving back of the ions into molecules by alcohol. — *American Chemical Journal*, vol. xviii., No. 5.

SILICIDE OF CALCIUM.

By G. DE CHALMOT.

WHEN making silicides of different metals in an electric furnace I have often used a flux in order to make the mixture that was used more liquid. In cases where I used lime as a flux, I have often found that the resulting silicide contains considerable amounts of calcium. I have thus introduced calcium in copper, silver, iron, and manganese silicide. I tried to obtain pure calcium silicide by putting into the furnace a mixture of silica, calcium oxide, and carbon. I have found that if these ingredients are mixed in such proportions as to give the compound CaSi_2 , mainly carbide of calcium is obtained, which, however, contains some silicide. If silica is used in excess, and the amount of carbon is reduced, a calcium silicide of metallic appearance can be obtained, especially if a direct current of low voltage (25 volts and 225 ampères) is used. This silicide often contains some carbide, as can be ascertained by the formation of acetylene gas. It also contains much more silicon and much less calcium than corresponds to the formula CaSi_2 . All my specimens, moreover, contain some iron. The iron is derived from the furnace, the pencils, and the silica (powdered quartz). All the iron which is present accumulates in silicide, because iron silicide is much more readily formed than calcium silicide.

Different samples contained:—

Calculated for CaSi_2 .		Found.			
		I.	II.	III.	IV.
Si ..	58.33	71.19	62.48	81.65	91.99
Ca ..	41.67	19.75	28.41	15.61	5.60
Fe ..	—	3.74	2.74	3.61	0.92

Specimens I. and II. contain calcium carbide, II. contains lead-coloured crystals imbedded in a more or less

crystalline matter. III. is silver-white, homogeneous, and of crystalline structure. IV. has much the same appearance, but is of darker colour and contains some graphite. It is remarkable that sample IV. was found on the anode, which was the upper pole in this special test. All specimens are hard enough to scratch glass.

The reactions which Wöhler describes (*Dammer: Anorganische Chemie* [2], ii., 327) for calcium silicide, CaSi_2 , were obtained with all the specimens.

With cold water some hydrogen is formed, more with warm water. Dilute hydrochloric acid forms a yellow silicic acid, and stronger hydrochloric acid forms a more orange-coloured acid. Dilute hydrochloric acid and sulphur dioxide form a red compound. I also found that if hydrochloric acid is brought into contact with finely-divided silicide, hydrogen silicide is sometimes formed, which is self-igniting, and when burning leaves little white flakes of silica.

In these specimens calcium silicide, CaSi_2 , and silicon are mixed. When they are boiled with hydrochloric acid, the calcium silicide is decomposed and crystals of silicon remain. A part of Sample III., which is apparently homogeneous, was thus treated. The insoluble residue of silicon and silicic acid was washed by decantation, and the silicic acid was dissolved with hot sodium carbonate solution. The remaining black crystals contained Si 95.88, and Fe 4.25 per cent.

This shows that these crystals contain, in addition to silicon, most of the iron silicide which is only a little attacked by boiling hydrochloric acid.

When calcium carbide is heated in an electric furnace with an excess of sand, some crystals are formed, which contain, in addition to silicon, some calcium silicide that can be detected by the hydrochloric acid reaction. — *American Chemical Journal*, vol. xviii., No. 4.

ON THE REACTION BETWEEN CARBON TETRACHLORIDE AND THE OXIDES OF NIOBIUM AND TANTALUM.

By M. DELAFONTAINE and C. E. LINEBARGER.

EUG. DEMARCAZ (*Comptes Rendus*, civ., III, 1887) states that if the vapour of carbon tetrachloride be passed over the oxide of niobium or of tantalum heated below redness, the metallic oxides are converted into chlorides. "Dans le cas de l'acide niobique, la réaction se produit déjà, bien qu'avec lenteur à la température de la naphthalène bouillante (280°) et avec une extrême rapidité à 440°." (*Loc. cit.*).

Now the chlorides of these rare elements enter into reaction very readily, and may serve as the starting-points for numerous syntheses. Demarcay's statements led us to believe that the reaction in question would furnish a rapid method of obtaining these chlorides in quantity with comparative ease. On making use of the method, however, we found that the reaction does not take place in just the way indicated by Demarcay. We will first communicate our results obtained with niobic acid.

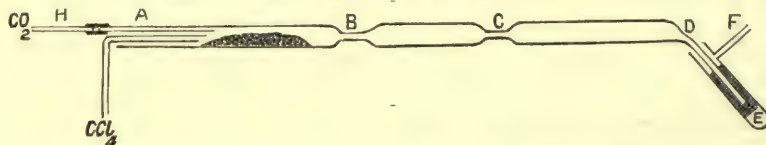
We used niobic pentoxide obtained from re-crystallised potassium oxyfluosalt resulting from treatments of samarskite. The salt was decomposed in the usual way by sulphuric acid, boiled with water, and the residue ignited at strong red heat to expel the last traces of sulphuric acid.

The oxide was placed in one end of a piece of hard glass tubing, constricted in several places (see Fig.), and the tube was heated in the vicinity of the oxide in a combustion furnace to 300°—400°. When the vapour of carbon tetrachloride was passed over the heated oxide, a reaction occurred immediately and a yellowish white sublimate condensed in the cooler parts of the tube. If

the oxide employed was quite pure, almost the totality of it could be converted into the volatile product. By careful application of heat it was possible to drive the sublimed substance into the further portions of the tube; it was then seen that the sublimate could be separated into two main portions, a more volatile one of a yellow colour, and a less volatile one of a nearly white colour. The properties of the yellow product were those of the pentachloride of niobium, while the properties of the whitish portion agreed with those of the oxychloride of niobium. By far the larger portion of the product of the reaction consisted of the oxychloride. The action of carbon tetrachloride on niobic acid seems to yield principally the oxychloride of niobium as the solid product; of the gaseous products formed, phosgene seemed to predominate.

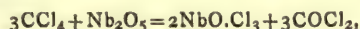
It was thought that possibly the presence of even a slight amount of air might exercise an oxidising influence upon the pentachloride at the moment of its formation, converting it into the oxychloride. We accordingly carried out the same experiment in an atmosphere of carbon dioxide, but could not see that the proportion of the pentachloride was at all increased.

Again it was considered that the relative amount of the pentachloride might be made greater by allowing the reaction to take place in an atmosphere of chlorine; but



even under such conditions the principal product was found to be the oxychloride.

We conceive, then, that the main reaction of carbon tetrachloride and niobic pentoxide may be represented by the equation—



which illustrates again the tendency that niobium has to enter into combination as *niobyl*.

We have prepared a considerable quantity of niobyl chloride according to the above reaction, and, after numerous experiments, have adopted the following method of conducting the operation:—

A tube of the shape indicated in the figure is prepared and filled with niobic pentoxide between A and B. As the chlorine compounds of niobium are quite voluminous, care has to be taken not to employ too much of the oxide; we found that for a tube of about 2 c.m. bore, and having a length of about 40 c.m. between A and B, 10 to 15 grms. could be taken. The tube is placed in a combustion furnace, and the portion in the vicinity of the oxide heated to about 400°. A current of dry carbon dioxide is now passed through the tube to dry it thoroughly and expel the air. The constrictions at B and C are heated nearly to redness to prevent their becoming stopped up, and carbon tetrachloride is gently distilled over upon the niobium compound. It is advisable to discontinue the current of carbonic acid by pinching the delivery tube together at H, since often the pressure of the tube becomes sufficient to throw the acid out of the generator. In the early stages of the operation there occurs a transportation of substance in such a fine state of division that it is carried clear through the tube: in order to prevent its entering the wash-bottle containing sulphuric acid, and connected at F, a little glass wool or asbestos fibre is packed around the end of the tube in E. When B C becomes nearly filled with the products of the reaction, it is heated to a temperature just sufficient to volatilise the pentachloride, which may then be driven over into C D, leaving almost pure oxychloride in B C. When the reaction is at an end, no more carbon tetra-

chloride is passed into the tube, but the current of carbon dioxide is again sent through it in order to aid in the separation of the pentachloride from the oxychloride of niobium. Any carbon tetrachloride that may have condensed in C D is driven over into E, and B C and C D are so heated that the pentachloride passes through the constriction C and condenses just in front of D. While it is possible to drive almost all of the pentachloride out of B C, and thus to obtain almost pure oxychloride, there is always a not inconsiderable portion of the latter compound that finds its way into C D.

In several experiments we found that a small quantity of an orange-coloured sublimate collected at the further end of C D, which circumstance proves that this substance is more volatile than the pentachloride of niobium. H. Rose (*Ann. Chem. Phys.*, Pogg., xcix., 75, 1856) also observed the formation of such a coloured product when he was engaged in the investigation of chlorine on an intimate mixture of charcoal and tantallic acid. He found that if the acid employed contained "nur die geringste Spur von Wolframsäure, so zeigt sich bei der Darstellung des Chlorids eine sehr kleine Menge von einem rothem Chloride, das etwas flüchtiger als das Tantalchlorid ist." The compound is probably the oxytetrachloride of tungsten, its formation being due to a slight contamination of our niobic acid with a tungsten compound.

When we passed the vapour of tetrachloride over tantallic acid, no reaction took place at a lower temperature than 400°, when a small amount of volatile substance was formed, which soon ceased, however. Even on heating to a temperature high enough to cause the Bohemian glass tube to soften, we did not obtain any more of the sublimable product. The tantallic oxide turned yellow and assumed a pasty condition. It is probable that the sublimed substance consisted of the chlorine compounds of niobium, since it is quite possible that our tantallic oxide was not entirely free from an admixture of niobic oxide. This behaviour suggests a method of purification of tantallic acid containing a little niobic acid: we will not lay much stress on this, however, until we have done more work on the subject.

The readiness with which niobium oxychloride was formed in all our experiments contrasting with the comparatively small quantity of the pentachloride obtained illustrates once again the great inclination niobium has to enter into combination, not as an individual element, but in the form of the radical *niobyl*. The action of sulphur and chlorine on NbO, investigated by Delafontaine, the numerous series of oxyfluor-salts prepared by Marignac, and the decomposition of niobyl chloride by magnesium, are other facts of the same import. In this respect the analogy of niobium and vanadium is very striking, but it is almost entirely lacking in niobium and tantalum. — *Journal of the American Chemical Society*, vol. xviii., No. 6.

On the Deep Blue Nitrosodisulphonic Acid.—Paul Sabatier.—Such an acid has never been previously obtained as that which the author has produced by dissolving a small quantity of dry sodium nitrite, which immediately reacts upon sulphuric acid, giving a very intense violet-blue colouration. The blue solutions thus obtained in sulphuric acid are gradually destroyed, but they are nevertheless much more stable than the anhydrous potassium salt of Fremy and Raschig. — *Compt. Rend.*, cxxii., No. 25.

A MODIFIED AMMONIUM MOLYBDATE SOLUTION.

By A. L. WINTON.

WHEN phosphoric acid is determined by the molybdate method, it is a common practice to add 15 grms. of ammonium nitrate to the phosphate solution and heat before adding ammonium molybdate. By this means the separation of the yellow precipitate is greatly facilitated and the time of digestion shortened. But to dissolve this nitrate requires some time and very greatly reduces the temperature of the solution, so that special care is necessary in heating it subsequently. In the laboratory of this station it has been our practice to simplify the process by omitting the separate addition of ammonium nitrate and using a molybdic solution containing the requisite quantity of the salt. Such a solution may be prepared according to the following formula:—

I. Dissolve 1000 grms. of molybdic acid in 4760 c.c. of a mixture of 1 part of concentrated ammonia water (sp. gr. 0.90) and 2 parts of water.

Dissolve 5300 grms. of ammonium nitrate in a mixture of 6250 c.c. of concentrated nitric acid (sp. gr. 1.4) and 3090 c.c. of water.

Add I. to II. slowly, with constant stirring. Allow to stand for a few days in a warm place, and decant off the clear liquid.

This solution has the same proportion of ammonium molybdate and free nitric acid as the molybdic solution of Fresenius, but differs from the latter in that *fifty c.c. contain fifteen grms. more of ammonium nitrate*. We have prepared the solution so as to contain this proportion of the salt, because in the routine analysis of fertilisers in the station laboratory 50 c.c. are most commonly employed. This quantity in our experience is usually sufficient for the precipitation of the soluble, insoluble, or total phosphoric acid of mixed fertilisers in solutions representing four-tenths, two, and five-tenths grms. respectively of the material.

In no case ought less than 50 c.c. be used, for otherwise there may not be enough ammonium nitrate present for the perfect separation of the yellow precipitate. When a larger quantity of molybdic solution is required,—as, for example, in the determination of total phosphoric acid in ground bone, bone-black, Thomas slag, &c.,—it may be added without fear that the larger quantity of ammonium nitrate contained in it will in any way interfere with the process. If, however, it is thought desirable, a special molybdic solution containing 15 grms. of added ammonium nitrate to every 75 or 100 c.c. of the liquid may be prepared for such cases.—*Journal of the American Chemical Society*, vol. xviii., No. 5.

ON THE CALCULATION OF THE CONDUCTIVITY OF MIXTURES OF ELECTROLYTES HAVING A COMMON ION.*

By DOUGLAS MCINTOSH,
Physical Laboratory, Dalhousie College, Halifax, N.S.

(Continued from p. 23).

Conductivities of the Simple Solutions.

In order to obtain the data for the calculations it is necessary to draw curves giving the relation of the dilution to the concentration of ions in the simple solutions, and therefore to know the concentrations and conductivities of sufficiently extended series of these solutions. In the case of sodium and potassium chlorides sufficient data were

available for this purpose in Kohlrausch's observations. The following tables give the dilutions and ionic concentrations of solutions of these salts examined by him.

Potassium Chloride.

Dilution.	Concentration of Ions.	Dilution.	Concentration of Ions.
2	0.3861	0.400	1.7311
1	0.7467	0.333	2.0328
0.666	1.0885	0.285	2.3131
0.500	1.4104		

Sodium Chloride.

Dilution.	Concentration of Ions.	Dilution.	Concentration of Ions.
2.30	0.3257*	0.500	1.1738
2.00	0.3689	0.400	1.3709
1.80	0.4036*	0.333	1.5378
1.64	0.4378*	0.285	1.6776
1.50	0.4732*	0.250	1.7920
1.20	0.5752*	0.222	1.8783
1.13	0.6109	0.200	1.9320
1.00	0.6777	0.182	0.9596
0.666	0.9456		

* Obtained through Prof. MacGregor's interpolation formula, *Trans. N. S. Inst. Sci.*, ix., 112.

In the case of hydrochloric acid sufficient data were not available. I therefore made a series of measurements of the concentrations and conductivities of solutions of this acid, the results of which are given in the following table:—

Concentration (Grm.-mols. per litre).	Molecular conductivity, $\times 10^8$.	Concentration (Grm.-mols. per litre).	Molecular conductivity, $\times 10^8$.
1.58	2550	2.80	2065
1.93	2403	2.88	2052
2.11	2347	3.15	1960
2.18	2305	3.29	1914
2.24	2290	3.39	1890
2.46	2245	3.60	1789
2.51	2192	3.83	1726
2.56	2164	4.13	1636
2.66	2141	4.55	1534
2.78	2090	4.87	1456

The following table contains values of the dilution and concentration of ions in hydrochloric acid solutions, obtained in part by graphical interpolation of the above observations, and in part by the aid of Kohlrausch's tables:—

Dilution.	Concentration of Ions.	Observed.
2.000	0.4310	Kohlrausch.
1.666	0.5090	"
1.428	0.5840	"
1.250	0.6567	"
1.111	0.7269	"
1.000	0.7943	"
0.800	0.9557	Observed.
0.666	1.1031	"
0.571	1.2370	"
0.500	1.3600	"
0.444	1.4660	"
0.400	1.5685	"
0.364	1.6516	"
0.333	1.7229	Kohlrausch.
0.286	1.8379	Observed.
0.250	1.9132	"
0.222	1.9746	"

The values of the specific molecular conductivity at infinite dilution for potassium chloride, sodium chloride, and hydrochloric acid respectively, were taken to be

* *Transactions of the Nova Scotian Institute of Science*, vol. ix., Session 1895-96.

1220×10^{-8} , 1030×10^{-8} , and 3500×10^{-8} according to Kohlrausch's determination (*Wied. Ann.*, xxvi., p. 204).

(To be continued).

HYDROFLUORIC ACID.*

By CARL F. STAHL.

HYDROFLUORIC acid is always made by decomposing ground fluor-spar with sulphuric acid in cast-iron vessels and absorbing the resulting fumes of hydrofluoric acid in leaden vessels of varying construction, containing more or less water, according to the strength desired.

The commercial acid, containing 40 to 52 per cent hydrofluoric, is stored and shipped in lead vessels, or small quantities in gutta-percha bottles. Weaker acid, of about 35 per cent and less, can be stored for a limited time in wood, and is sometimes shipped in barrels, usually oil barrels. In the United States the so-called "chemically pure" acid is packed in ceresine bottles, which answer very well, but must be kept away from the Bunsen burner, as the melting-point of the ceresine is low. In Europe the C.P. acid is shipped either in gutta-percha or platinum bottles, but the acid takes up, in course of time, mineral and organic matter from the gutta-percha and ceases to be C.P. Platinum bottles are the best, but require a heavy investment.

The impurities, which can hardly be avoided in manufacturing commercial hydrofluoric acid, and are therefore always present, are:—

1. *Hydrofluosilicic Acid*.—This is the most important impurity, not because it does any direct harm in the application of the acid, but because the fluorine combined with silica is perfectly useless. The source of the hydrofluosilicic acid is free or combined silica in the fluor-spar, which is all dissolved and volatilised by the hydrofluoric acid. It seems almost impossible to obtain spar free from silica. American ground fluor-spar contains usually about 1 per cent; samples of English spar which I have tested, were even higher in silica, about 3 per cent; whilst six samples of German spar contained from one-tenth to seven-tenths per cent silica. In the rapid determination of silica in fluor-spar, an analytical problem presents itself, which I have not yet solved to my satisfaction. I use the following extremely simple method:—

One grm. of ground fluor-spar, in a platinum dish, with a small platinum spatula, is dried at about 130°C ., weighed exactly, moistened with hydrofluoric acid, stirred with a spatula, evaporated to dryness on the water-bath; this is repeated, then dried again at 130°C ., and weighed. The difference I assume to be silica, which is only correct when free silica is present, but the spar may contain silicates—for instance, clay; in that case, a fluoride of aluminum would be formed, part of the weight of the silica would be replaced by the weight of the fluorine retained, and the silica be found too low. If carbonates are present the error would not be great, for instance,—

CaCO_3 (100) would give CaF_2 (78).

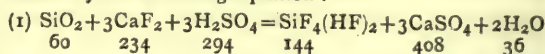
and the silica be found too high. The presence of carbonate is, however, easily detected, and the carbonate can be removed with acetic acid. Galena is often present in small quantities and gives the spar a greyish or bluish colour; in that case—

PbS (239) would give PbF_2 (245),

an error that would not be perceptible. This simple method, to which any careful boy can be drilled in a short time, is therefore likely to give quite accurate results.

* Abstracted from a Lecture before the Chemical Section of the Engineers Society of Western Pennsylvania, at Pittsburgh, February 28th, 1896. From the *Journal of the American Chemical Society*, xviii., No. 5.

The great damage done by silica in the spar is plainly shown by the following equation:—



For every part of silica about 4 parts of fluor-spar and 5 parts of sulphuric acid are wasted, or expressing it in money value, for every per cent of silica at least 10 per cent (4 per cent for spar and about 7 per cent for sulphuric acid) should be deducted from the value of the spar.

2. *Sulphuric acid*, which is distilled over in small quantities out of the decomposing vessel, does no harm in the application of the hydrofluoric acid for etching glass or pickling iron. But in analysing the acid it must be determined, otherwise it would be figured as hydrofluoric acid.

On evaporation and calcining, commercial acid should leave but a trace of non-volatile matter.

About five years ago, having made some hydrofluoric acid in an experimental apparatus, I was confronted with the inability to tell what I had made; that is, I could not find a method which would have enabled me to determine the composition in a reasonably short time.

The method of determining quickly the percentage of a liquid by its specific gravity is of little value for two reasons; first, because the methods for determining the sp. gr. of other liquids can only be used with modifications for hydrofluoric acid, as they involve the use of a glass instrument of some kind. A glass hydrometer can only be used a few times until the acid has ruined it; picnometers are out of the question; even the temperature of hydrofluoric acid cannot be determined directly with a thermometer, as soon as a glass thermometer is placed into the acid the mercury begins to rise from the heat evolved by the action of the acid on the glass. I use, therefore, a platinum hydrometer. A hydrometer made from pure silver would probably last a long time. I have seen one made out of German silver plated with silver, but the hydrofluoric acid got through the plating and ate numerous pinholes into the instrument.

The impurities mentioned above, i.e., hydrofluosilicic acid and sulphuric acid, influence the specific gravity of the hydrofluoric acid to a marked degree, so much that the determination of the specific gravity of an acid of unknown origin is of little value, but for controlling the process in the works, where the character of the raw materials and the degree of purity of the produced hydrofluoric acid is known, it is of value, provided the conclusions drawn from it are from time to time verified by an analysis. It will not do to depend too much on the specific gravity.

Without taking up any time with a description of the experiments, which led finally to the method I use, I will give the latter in detail.

The samples are brought to the laboratory in lead cylinders of convenient size, with a handle. These are placed in water of 15°C ., often remaining there for at least five minutes; the specific gravity is taken; then with the aid of a small platinum tube, serving as a pipette, and chips of filtering paper, to remove a small excess, three portions are weighed out:—

1. Two grms. in a very small platinum crucible (holding about 5 c.c.).

2. Two grms. in a large platinum crucible (holding about 40 c.c.).

3. Four grms. in a small platinum dish.

A.—Total Acidity.

Place the small platinum crucible, covered with its lid, in a large platinum dish (holding about 100 c.c.), then run according to the expected percentage, 25 or 50 c.c. normal caustic solution (40 grms. caustic soda per litre) from a pipette into the dish, upset the covered crucible, and mix the acid and alkali with a platinum stirrer; add 2 drops of a solution of phenolphthalein (1 grm. in 100 c.c. alcohol), and then add more of the normal soda solution from a burette till the colourless liquid assumes the

characteristic bright red colour. Place over a Bunsen burner and heat to about 50° C.; the red colour will disappear. Finally add normal solution from the burette slowly till the red colour remains constant when heated, which indicates that all free sulphuric acid, hydrofluoric acid, and hydrofluosilicic acid have been neutralised. The number of c.c. used we call "a."

If litmus is used in place of phenolphthalein, the soda solution has to be added till the colour is perfectly blue, but the end of the reaction is indistinct, while with phenolphthalein as indicator it is very sharp.

B.—Hydrofluosilicic Acid.

To the acid in the large platinum crucible (2 grms.) add 5 c.c. water (measured approximately); then slowly about 2 grms.* potassium carbonate either in small pieces or in concentrated solution, add about 15 c.c. of 50 per cent alcohol, and then as many c.c. of 95 per cent alcohol as water used, which will bring the whole to a volume of about 25 c.c. containing about 50 per cent alcohol;† let it stand for at least one hour. Filter‡ and wash the gelatinous precipitate, consisting of potassium silicofluoride, with 50 per cent alcohol till blue litmus paper ceases to be turned red by the filtrate. Throw the filter with the precipitate into a platinum dish, add about 25 c.c. of water, and warm to about 50° C.; titrate slowly with normal caustic soda solution and phenolphthalein, as described in the determination of total acidity. The number of c.c. used we call "b."

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 25, June 22, 1896.

The Academy proceeded to the nomination of a correspondent for the section of Astronomy, *vice* the late Prof. Cayley. Mr. Gill obtained the unanimity of the votes and was elected.

Formation of Gaseous and Liquid Hydrocarbides by the Action of Water upon the Metallic Carbides. Classification of Carbides.—Henri Moissan.

Letter by Armand Gautier accompanying the Presentation of his Work on the "Animal and Microbian Toxines."—Toxines are poisons secreted by microbia or formed by the animal economy which, if introduced into our organs or not completely eliminated, bring on a pathological state and involve profound and often permanent modifications of the nutrition and of the vitality of the cellules. These toxines are of three kinds: *a*, The *Pto-maines*, definite alkaloidal poisons formed by the microbia; *b*, *Leucomaines*, basic substances, definite like the foregoing, but which are formed in our organs themselves in the regular course of life; *c*, *Toxines, properly so called*, poisons either albumenoid or of an indeterminate chemical

nature, playing in general the part of ferments of a surprising activity. They are secreted by pathogenous microbia as well as by venomous animals and by certain plants. They form the essentially injurious portion of venoms and virus. The successive and detailed study of these three orders of poisons forms the principal divisions of this work. Along with the microbian toxines I describe the soluble ferments, animal and vegetable, the specific glandular secretions as well as those curious *antitoxines* which the living organism produces when it reacts and defends itself against the attacks of those dangerous agents. These are the antitoxines now utilised in *serotherapy*. At the moment when it was recognised that the direct causes of sickness and of return to health reside in the action of the poisons, ferments, and counterpoisons secreted by the microbia or by the organism itself, it was natural to ask what are the *toxines*, these *ferments*, and these antitoxines, to describe them, and to try to account for their inward nature. This is what I have attempted in the work just published.

On the X Rays.—C. Maltzós.—If experiment demonstrates that the refraction of the X rays is not strictly null the radiations are transverse and of an infinitely small wave-length. These are hyper-ultra-violet rays, and the conclusions of the author's former memoir must be maintained. If, on the contrary, the refraction is absolutely null we may conclude that $\lambda = 0$, for in this case all the optical properties are theoretically demonstrated; they are terminal radiations. But until this is experimentally demonstrated we must not reject the existence of the hyper-ultra-violet rays. They must exist.

Procedure of Electrolytic Disargention of Argenterous Lead.—D. Tommasi.—Will be inserted in full.

Preparation of the Alloys of Aluminium by a Chemical Reaction.—Charles Combes.—Will be inserted at some length.

Action of Phosphorus on certain Metallic Chlorides.—A. Granger.—Nickel and cobalt chlorides behave like ferrous chloride. At a dull red heat phosphorus converts them into nickel and cobalt sesquiphosphides. It is important not to operate at too high a temperature. The sesquiphosphides are not magnetic.

Measure of a Heat of Etherification by the Action of a Chloride of Acid upon Sodid Alcohol.—J. Cavalier.—A thermo-chemical paper not suitable for abstraction.

On Acetal and Monochloric Acetal.—Paul Rivals.—The substitution of chlorine in aldehyd does not seem to have any appreciable thermic influence upon the formation of the ethylic derivatives of ethyl.

Ethylic Ethers of the Chloric Acetic Acids.—Paul Rivals.—A thermo-chemical paper not suitable for abridgement.

Action of Hydrazines upon the Glyoxylic Acids of the Aromatic Series.—L. Bouveault.—In order to regulate the decomposition of these glyoxylic acids into aldehyds and carbonic acid the author has sought to transform their carbonyl into a more solid grouping. To this end he has made use of hydrazin.

Constitution of Inactive Campholenic Acid.—MM. Guerbet and Bèhal.—If we set aside the indications given by oxidation, the formula of camphor, as results from our experiments and as proposed by Bouveault, explains the facts well.

Rational Denaturation of Alcohol.—G. Jacquemin.—A single drop of the indifferent sulphuretted oil of Zeiss added to a litre of alcohol at 90° renders it permanently unfit for human consumption. It is the cheapest denaturing agent, cannot be precipitated by any reagent, and does not interfere with any of the industrial applications of alcohol.

Chemical Mechanism of the Reduction of Nitrates and the Formation of Quaternary Nitrogenous

* The amount of potassium carbonate is calculated to neutralise the acids only partly. To avoid an excess it is advisable to test the liquid with litmus paper, which should show a strong acid reaction. But there should be at least enough potash to form potassium silicofluoride with the fluosilicic acid. In analysing acid of entirely unknown composition, I take for every c.c. normal soda solution used for the determination of total acidity 0.05 grm. potassium carbonate. Potassium chloride might be used in place of the carbonate, but in that case free hydrochloric acid is formed, in which the potassium silicofluoride is somewhat soluble.

† If the liquid contains more than 50 per cent alcohol, potassium fluoride is precipitated; if much less alcohol, potassium silicofluoride may remain in solution.

‡ I use a platinum funnel because glass funnels are acted on, but it does not influence the accuracy of the method.

Matters in Plants.—A. Bach.—Formaldoxime constitutes first quaternary term of the reduction of nitric acid by formic aldehyd.

Nutritive Value of Flours, and on the Economic Consequences of Excessive Sifting.—M. Balland.—A defence of coarse flours.

Zeitschrift für Analytische Chemie.
Vol. xxxv., Part 1.

Preparation of Strong Solutions of Hydrogen Peroxide.—P. Schiloff (*Journ. Soc. Phys. Chim. Russe de St. Petersburg*, 1893, No. 5).—The author, like Crismer, utilises the solubility of the peroxide in ether. He mixes the commercial product with sodium carbonate until a distinct alkaline reaction is obtained. He filters and shakes up the liquid with 10 to 12 vols. of ether for three to five minutes. The ethereal solution is then lifted off and separated on the water-bath, to expel the chief quantity of ether. The residue is expelled on a paraffin-bath. During these operations but little peroxide is lost. The product obtained contains about half the peroxide present in the original solution. It contains no mineral acid, is not rendered cloudy by silver nitrate, and gives with barium chloride a precipitate perfectly soluble in hydrochloric acid. It is colourless, only has a distinct acid reaction, and has the specific gravity 1.1756. It contains 54 per cent H_2O_2 . If concentrated to 1.2475, the solution contains 79.57 per cent H_2O_2 , and has a slight yellowish colour.

Volumetric Determination of Chloroplatinates; Determination of Potassium, Ammonia, Nitrogen, and Platinum.—(*Chemiker Zeitung and Comptes Rendus*).

Influence of certain Platinum Metals upon the Accuracy of Results obtained in Quantitation of Gold.

Quantitative Determination of Molybdenum.—C. Friedheim and H. Euler (*Berichte, Comptes Rendus, and other Journals*).

Volumetric Determination of Molybdenum Trioxide and Vanadium Pentoxide.—Milch, Liebert, Friedheim, Euler, Holverscheid.

A Simplified Method of Determining Phosphoric Acid by means of Molybdic Solution.—J. Hanamann (*Chemiker Zeitung*).—Already inserted.

Detection of Alkaline Perchlorates in presence of Chlorides, Chlorates, and Nitrates.—A. Gooch and Albert Kreider (*Zeit. Anorg. Chemie*).—Already inserted.

An Introduction to the Micro-chemical Analysis of Organic Compounds.—H. Behrens.—No details are given.

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1913.

ON THE EFFECT OF MOLECULAR BOMBARDMENT ON THE DIAMOND.

By WILLIAM CROOKES, F.R.S.

In view of the great interest attaching to the diamond, in consequence of the brilliant researches of M. Moissan on its artificial production, it may be useful to put on record some old observations I made connected with the behaviour of this stone when submitted to molecular bombardment in a vacuum tube under the influence of the secondary current from an induction coil. In 1879* I published the fact that diamonds phosphoresced of various colours when treated in the above-mentioned manner, and since that date the phosphorescence of the diamond has been repeatedly exhibited.

During molecular bombardment the diamond becomes discoloured, and in course of time becomes black on the surface.† Some diamonds blacken in the course of a few minutes, while others require an hour or more to discolour. This blackening is only superficial, and although no ordinary means of cleaning will remove the discolouration, it goes at once when the stone is polished with diamond powder. Ordinary oxidising reagents have little or no effect in restoring the colour. I consider the following is a reasonable explanation of the phenomenon:—

It is well known that great heat has the effect of converting diamond into graphite. In a paper published in 1891, I showed that in a vacuum tube a silver pole had the appearance of being red-hot, while the volatilisation of the metal proceeded rapidly.‡ This "red heat" is superficial only. The metal instantly assumes, or loses, the appearance of red heat the moment the current is turned on or off, showing that, if the appearance is really due to a rise of temperature, it does not penetrate much below the surface. The extra activity of the silver molecules necessary to volatilise them is in these experiments confined to the surface only, and is probably less than would be the case with a bad conductor of heat, such as the diamond. In the case of diamond, the electrical and molecular excitation which is capable of raising the superficial layer of silver molecules to redness, heats or excites the outer layer of carbon molecules sufficiently to convert them from diamond to graphite.§

I have said the black stain on the diamond is not affected by ordinary oxidising reagents. This would seem to show that it is not due to a layer of amorphous

carbon; but it might be graphite, which is much more resistant to oxidation. Becquerel has shown that graphite is converted into graphitic oxide by long digestion in a warm mixture of potassium chlorate and strong nitric acid, while diamond—even in a very finely-powdered state—is absolutely unaffected by the mixture.* I accordingly tried the following experiment:—Three diamonds of a good white colour, and approximately of the same size, were selected from a parcel I brought from the Kimberley Mine in April last. One was set aside for comparison, while the other two were bombarded in a vacuum tube for five hours. At the end of that time they were well blackened superficially. One of these discoloured stones was also set aside for comparison, while the other was digested for three days in a mixture of potassium chlorate and strong nitric acid at a temperature of about 50° C. An exactly similar experiment was performed with three bright yellow diamonds from the Wesselson Mine, Kimberley.

At the end of the three days' digestion the reagent was washed away and the diamonds examined. Not only was the superficial blackening entirely removed, but on comparing the cleaned diamonds with the original ones which had been at first set aside, they had, if anything, appreciably more brilliancy. This proves that the black stain on the surface is produced by the conversion of the superficial layers of molecules from diamond to graphite. Microscopic examination under high powers fails to show any alteration of the smooth crystalline surface either before or after the blackened diamonds have been treated to the chemical reagents.

It is not necessary to expose the diamond in a vacuum to electrical excitement in order to produce a change. Some diamonds phosphoresce when exposed to the sun's rays or to an electrical discharge in the air, and many more are phosphorescent when exposed to the Röntgen rays. In the latter cases a slight superficial blackening also takes place.

On recently examining some diamonds sealed up in a vacuum tube and considerably blackened many years ago, I am inclined to think that they are by no means so dark as they were when they were being frequently exhibited. It is not beyond credibility that a renovation may take place in the course of time and rest. The molecules of diamond are in a state of constant motion. Those constituting the body of the diamond vibrate in a manner different to the converted graphite molecules forming the superficial layers. It is not so very unlikely that the whole mass of crystalline diamond vibrating in one manner may so hamper the movement of the comparatively infinitesimal number of graphite molecules vibrating in another direction that the latter may gradually be constrained to take on themselves the same kind of motion as the crystal itself is engaged in, and so become ultimately re-converted from graphite to diamond.

ON THE BEHAVIOUR OF RÖNTGEN'S RAYS.

By C. DOELTER.

THE behaviour of Röntgen rays with minerals has been carefully examined by the author, with especial reference to their density and chemical composition. The Röntgen rays are especially important as a means for distinguishing precious stones from doublets. The transmissibility of a mineral for the Röntgen rays is not connected with its density; only the very heavy species (above 5) being non-transmissive. Among light minerals, rock-salt, sulphur, potash, saltpetre, and realgar are non-transmissive; among heavy minerals, cryolite, corundum, and diamond are quite transmissive. In many silicates the introduction of iron in place of aluminium occasions non-trans-

* "Most of these gems (diamonds), whether cut or in the rough, when coming from the South African fields, phosphoresce of a brilliant bright blue colour. Diamonds from other localities shine with different colours, such as bright blue, pale blue, apricot, red, yellowish green, orange, and bright green. One beautiful green diamond in my collection, when phosphorescing in a good vacuum, gives almost as much light as a candle; the light is pale green—almost white. A beautiful collection of diamond crystals, kindly lent me by Professor Maskelyne, phosphoresces with nearly all the colours of the rainbow, the different faces glowing with different shades of colour."—*Phil. Trans.*, Part II., 1879, p. 660.

† *Phil. Trans.*, Part II., 1879, p. 658, par. 625.

‡ *Proc. R. S.*, vol. I., p. 99, June, 1891, "On Electrical Evaporation."

§ In other cases, also, long-continued molecular bombardment has the effect of profoundly altering the physical state of an amorphous powder. Some chemically pure alumina sealed up in a vacuum tube in 1879 was originally snow white; but after being frequently submitted to the molecular discharge for the purpose of exhibiting its brilliant phosphorescence, it gradually assumed a pink tinge, and on spectroscopic examination in sunlight a trace of the crimson alumina line could be seen. The repeated molecular excitation has slowly converted the amorphous powder to a crystalline form.

* *Ann. de Chim. et de Phys.*, 4, xix., p. 392.

missiveness, whilst compounds of boron and aluminium are more transmissive, and arseniates and phosphates keep back the rays. A general dependence on chemical composition can no more be shown than on molecular weight and on density. Dimorphous minerals show, for the most part, scarcely perceptible differences in transmissibility, only such differences are more perceptible in rutile and brookite, pyrites and marcasite, calc-spar and arragonite. If the rays are thrown through crystals in different crystallographic directions, the differences observed were unimportant, as in andalusite, diamond, and quartz. Among the transmissive minerals rank diamond, boric acid, amber, corundum, meerschaum, kaolin, asbestos, and cryolite; among the non-transmissive are epidote, cerussite, baryta, pyrites, arsenite, rutile, valentinite, and almandine. The author recognises eight groups the several members of which showed little difference in transmissiveness, though they differed strongly from each other:—(1) Diamond; (2) corundum; (3) talc; (4) quartz; (5) rock-salt; (6) calc-spar; (7) cerussite; (8) realgar.—*Mittheil. d. Naturw. Vereins für Steiermark*, 1895, and *Chemiker Zeitung*.

PROCEDURE FOR ELECTROLYTIC DESILVERING ARGENTIFEROUS LEAD.

By D. TOMMASI.

THE principle on which this procedure is founded consists in electrolysing a lead solution which not merely possesses an extremely weak electric resistance, but does not give rise to lead peroxide (PbO_2), and, in taking the argentiferous alloy itself as anode and as kathode, a metallic disc which cannot be attacked by the bath.

Under the action of the current the lead of the anodes enters into solution, and is transferred, in the state of spongy crystals, upon the disc which serves as kathode, whilst all the silver contained in the lead, being insoluble in the bath, is deposited at the bottom of the vat in a perforated receiver destined for its collection.

The following is the course to be followed for the electrolytic extraction of silver from argentiferous lead:—

We melt the lead, and then cast it in moulds having the shape and the thickness which is intended for the anodes. This being done, we suspend each anode to one of the two metallic poles which are found placed about the upper part of electrolyser.

Each metal pole is fitted with an endless screw and with nuts. At the ends of these poles are fixed plugs intended to connect the anodes electrically among themselves, and to secure the whole to the positive pole of the dynamo.

The object of this arrangement is not merely to keep the electrodes at a determined distance from each other, but to approximate them if this distance becomes too great in consequence of the progressive wear of the anodes.

The disc which serves as kathode is placed between the two anodes, and communicates with the negative pole of the dynamo by means of a metal brush rubbing upon its axle.

The electrolyser being fitted up we pour in the bath (a solution of the double acetate of lead and sodium or of lead and potassium), close the circuit, and cause the disc to revolve at the rate of one or two rotations per minute.

When the current is established, the lead begins to deposit upon the disc in the form of small spongy crystals. When the deposit of lead has acquired a sufficient thickness, and it is thought suitable to remove it, the current is interrupted and the scrapers closed.

In consequence of their friction against the faces of the disc, the lead is detached and falls into sloping gutters, which bring it upon a sieve of metal cloth. The lead is

drained, washed with distilled water, and then submitted to a strong pressure.

The liquid which flows off is added to the washing-waters, and the whole evaporated down to 30° Baumé. When cold, this liquid is introduced into the electrolysers by means of a pump. The compressed lead is heated on a crucible with 2 to 3 per cent of charcoal in powder, and when melted it is cast in ingots.

When the anodes are dissolved, we may either replace them with fresh anodes, or merely withdraw the silver deposited at the bottom of the vat. In this latter case we raise the disc by means of a windlass; then withdraw the perforated recipient placed at the bottom of the vat at the beginning of the operation; this contains all the silver left behind by the argentiferous lead of the anodes.

The silver, when collected, washed, and dried, is melted in a crucible with sodium nitrate and a little borax, and is then cast in ingots.—*Comptes Rendus*, cxvii., p. 1476.

THE DETECTION OF MERCURY IN CASES OF POISONING.

By D. VITALI.

THE recognition of mercury, in general rather easy, may yet become doubtful if the poison is only present in fractions of m.grms. In such cases the expert should content himself with carrying out one or two of the most characteristic reactions.

After the destruction of the organic matter, according to the Fresenius-Babo method, the filtrate is evaporated as far as possible without separating potassium chloride or the supposed potassium mercury chloride in crystals. A current of sulphuretted hydrogen is passed for a rather long time through the solution, which is then allowed to stand for some hours in a moderately warm place. The mercury sulphide, after settling, is repeatedly washed by decantation, then dried in a porcelain capsule on the water-bath, and dissolved in *aqua-regia*. The solution is freed from free chlorine and nitric acid by evaporation with the addition of hydrochloric acid. The residue consists of mercuric chloride, and is decomposed electrolytically. In place of the methods of Smithson, of Danger and Flaudin, or Mayençon (which have been hitherto used, but are not sufficiently sensitive, often erroneous or too tedious), the following procedure may be successfully used:—

The supposed solution of mercury is put in a minute porcelain capsule, in which are immersed small pieces of sheet-gold and small iron tacks. The mercury present in solution deposits itself upon the gold, and, according to the author's experiments, partly upon the iron nails. After about an hour, when the deposition of the mercury is probably complete (which may be easily ascertained by testing a drop with a drop of sulphuretted hydrogen water), the fragments of the two metals are removed from the liquid, washed with water, dried with filter-paper, and heated to faint redness in a test-tube about 6 c.m. in length and 6 m.m. in width. The mercury forms a grey coating near the heated part of the glass. The fragments of gold and the iron nails are then taken out; a crystal of iodine is put into the tube, which is gently heated. The iodine vapours in contact with the mercurial coating form at first a yellow ring, passing into red (mercuric) iodide. If the iodine is used in excess there is formed a brown ring. By this process 0.00001 grm. of mercury can be recognised.

The mercury deposited on the metals may also be shown by placing the washed and dried portions of gold and iron in a porcelain capsule, covered with a small inverted porcelain capsule moistened with solution of gold chloride, heating the lower capsule then on the water-bath. However minute a quantity of mercury has been attached to

the metals, the inner surface of the upper capsule displays a violet-blue colour, owing to the reduction of gold occasioned by the mercurial vapours.—*Chemiker Zeitung*.

ON THE SPECTRUM OF PHOSPHORUS IN FUSED SALTS, AND ON CERTAIN METALLURGICAL PRODUCTS.

By A. DE GRAMONT.

THE fused phosphates, submitted to the action of the condensed spark according to the arrangement which I have already employed for other salts (*Comptes Rendus*, July 8, 1895, and June 8, 1896) give a very beautiful spectrum of the lines of phosphorus, easy to obtain, and superior in definiteness and in luminous intensity to that of the Plücker phosphorus tubes. I have thus resumed the study of the spectrum of this element, formerly undertaken by M. Salet, with a less dispersion and in different conditions, an explanation of which will be found in the author's "Traité de Spectroscopie."

I have principally made use of melted sodium phosphate and potassium phosphate; and on cutting off from the spectrum given by these salts the sodium and potassium rays mentioned in a former memoir (*Comptes Rendus*, June 15, 1896), I have obtained the following wave-lengths for the line spectrum of phosphorus:—

	650.6	Diffused.
	645.8	Well-marked.
	608.8	Quite visible; not seen by Salet.
a.	604.2	Strong, bright.
	603.45	Rather strong, fine.
	602.5	Strong, bright.
β.	549.85	Quite well visible.
	546.2	Feeble
	545.3	Feeble.
γ.	542.35	Very strong.
	540.9	Strong; not seen by Salet.
	538.5	Strong; not seen by Salet.
	534.0	Strong, rather diffused; not seen by Salet.
	531.1	Strong.
	529.2	Strong.
δ.	525.0	Very strong.
	496.8	Very well visible, diffused; not seen by Salet.
	494.1	Well-marked.
e.	460.3	Very strong.
	458.85	Very strong.

The alphabetical designations of the rays are those of Salet.

There is little difference of intensity between the rays marked as *strong* and those marked *very strong*.

The rays most easily recognised, from their position and their aspect, are—the triplet P α in the red and the doublet P β in the blue, and then the green rays from P γ to P δ . Three of the latter have not been seen by Salet, but they correspond in intensity and nearly in position with the lines appearing on a plate of Plücker's memoir, from which their wave-length has been approximately reduced by Watts. Besides, the spectra published by Plücker, and then by Salet, had been produced by tubes containing either vapour of phosphorus at a reduced pressure, or phosphorus chloride from which the rays of chlorine had been eliminated, therefore in conditions differing as to pressure and temperature.

The spectrum of phosphorus which I have just given is not peculiar to the melted salts. I have recognised it also, in the cold, in phosphoretted metallurgical products, which, having been submitted to direct spectral examination in the condensed spark with my arrangement for the

study of minerals ("Analyse Spectrale Directe des Minéraux": Paris, 1895), show easily, among the rays of the metal, those also of phosphorus. These latter are especially visible and brilliant in the copper phosphides, where the metallic rays are not very numerous. In phosphoretted cast-irons the multiplicity of the rays of iron would render the recognition of those of phosphorus more difficult if the triplet P α did not stand out very brightly in the red. This effect has been very characteristic and persistent in a cast-iron containing 2 per cent of phosphorus courteously sent me by M. Meyer, manager of the works of Dudelange (Luxembourg). An iron phosphide, extracted by M. Friedel from the meteorite of the Cañon Diablo, has also yielded the principal rays of phosphorus. I have since pursued the research for the latter in the cast-irons analysed at the Assay Office of the Ecole des Mines, kindly placed at my disposal by M. Adolphe Carnot. I have found that the presence of the triplet P α , more and more transient with the decrease of the proportion of phosphorus in the metal, became almost invisible within limits comprised between one-hundredth and one-thousandth.

For other non-metals, also, it seems to me that the duration of the appearance of their spectrum in metallic compounds, minerals, or fused salts is, if not proportional to the quantity of the non-metal, at least a function of the latter. Perhaps we may here find a basis for new attempts in spectral quantitative analysis.—*Comptes Rendus*, cxvii., p. 1534.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1896.

By WILLIAM CROOKES, F.R.S.,

and

PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, July 11th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month of June shows an excess of 0.31 inch, the total actual fall being 2.42 inches (occurring on ten days only), whereas the thirty years' average fall is only 2.11 inches.

Of this amount of rain 1.94 inches fell from the 4th to the 10th, inclusive.

There is still a large deficiency of rain for the year, viz., 4.38 inches.

Our bacteriological examinations gave the following results:—

	Colonies per c.c.
Thames water, unfiltered	2081
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	70
Ditto ditto lowest	2
Ditto ditto .. (12 samples) mean	32
New River water, unfiltered	836
New River water, from the Company's clear water well	35
River Lea water, unfiltered	1729
River Lea water from the East London Com- pany's clear water well	28

A comparison of our figures shows that, in spite of the sudden excess of rain after a prolonged drought, the Companies have effectively coped with the additional amount of extraneous matter brought down by the flood waters.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

A STUDY OF THE ZIRCONATES.*

By F. P. VENABLE and THOMAS CLARKE.

THIS class of compounds of zirconium has received but little attention from chemists. The chief investigator in the past who has worked in this field was Hiortdahl (*Ann. Chem. Pharm.*, cxxxvii., 34, 236). Of recent years several papers by L. Ouvrard (*Comptes Rendus*, cxii., 1444-46, and cxiii., 1021-22) have appeared. The accounts given in the various text-books of these zirconates are based upon the work of Hiortdahl, or upon such abstracts of it as were to be found in the *Fahresberichte*, or in such dictionaries as that of Watts. This is unfortunate, as to the best of our knowledge the work of Hiortdahl itself is in some respects inaccurate and erroneous, and the abstracts of it are misleading. Before giving an account of our own experiments, it may be well to gather together the statements regarding these bodies as given by Watts and in the original article of Hiortdahl.

Watts says that the compounds of zirconia with the stronger bases are obtained by precipitating a zirconium salt with potash or soda, also by igniting zirconia with an alkaline hydroxide. "Zirconate of potassium thus obtained dissolves completely in water." His first mode of preparing the zirconates is very questionable; the last statement is not true. He then goes on and describes zirconates of sodium, calcium, and magnesium, as described by Hiortdahl. The details of Hiortdahl's analyses, &c., will show on what an imperfect basis the knowledge of the constitution of these bodies rests. Hiortdahl states that he secured direct union only by ignition with alkaline carbonates. His attempts with the volatile chlorides failed. On heating zirconia with sodium carbonate one equivalent of carbon dioxide was driven out, and it is on the loss of carbon dioxide upon ignition that his figures for the composition of the resulting products are largely based. On heating equivalent amounts of zirconia and sodium carbonate a crystalline mass was obtained, which slowly absorbed moisture from the air. On treating this with water no decomposition was noted at first, but soon the water became alkaline and zirconia separated. This was taken as proof that the zirconia was decomposed by the water. In the experiment 0.3910 grm. zirconia heated with 0.3130 grm. sodium carbonate to a dark redness for nine hours lost 0.1310 grm. carbon dioxide, and on treatment with water 0.3871 grm. "zirconia," or 99.03 per cent was left. If an

excess of sodium carbonate is used one can drive out two equivalents of carbon dioxide. A little further down he notes that the "Gewichtsverlust zugleich von der Temperatur und der Dauer des Glühens abhängt." These are the determinations from which formulæ for the zirconates are worked out.

It is scarcely necessary to say that for purposes of calculation these figures are entirely worthless. The loss of carbon dioxide is due to a partial formation of hydroxide as well as to a combination with zirconia. The fused mass of sodium carbonate, hydroxide, zirconate, and unchanged zirconia will of course prove hygroscopic, and water will wash away all except the last two mentioned. We have failed to get any positive evidence that a zirconate formed by fusion was decomposed by water or was appreciably soluble in it.

In his second paper, Hiortdahl treats the fused mass of zirconia and sodium carbonate with water acidified with hydrochloric acid, and analyses the residue, finding in it ZrO_2 , 78.54 per cent; Na_2O , 5.40 per cent; and H_2O , 16.89 per cent; corresponding to $\text{Na}_2\text{O} \cdot 0.8\text{ZrO}_2$. He gets the zirconate of magnesium and calcium by fusing zirconia and silica with magnesium chloride and calcium chloride respectively.

Ouvrard obtained his zirconates by fusions with the chlorides, also using those of lithium, calcium, strontium, and barium. In some cases, instead of using zirconia, he took powdered zircons, obtaining silico-zirconates.

In our own experiments the following methods of forming the zirconates were tried:—

- I. Fusing in boron trioxide, the zirconia and the basic oxide (Ebelmen).
- II. Fusing zirconia with alkaline carbonates (Hiortdahl).
- III. Fusing zirconia with alkaline hydroxides.
- IV. Fusing zirconia with alkaline or earthy chlorides (Hiortdahl).
- V. Precipitation of solutions of zirconium salts with alkaline hydroxides (Watts).
- VI. Dissolving zirconium hydroxide in strong solutions of sodium or potassium hydroxide, and precipitation by dilution or by neutralisation with an acid.

I. Fusion with Boron Trioxide.

This method, made use of by Ebelmen in the case of other oxides, is useless in the case of zirconia, because this oxide is not taken up by the boron trioxide, and so does not come in contact with the other oxide. The melt of boron trioxide was kept at a high temperature for a number of hours without any appreciable solvent action upon the zirconia, added in small portions.

II. Fusion of Zirconia with Alkaline Carbonates.

The purified zirconia used had been dried at the temperature of the steam-bath, and therefore was not in the inactive condition brought about by igniting it at a very high temperature. This was the case in the subsequent experiments also.

It is by fusion with sodium carbonate that Hiortdahl claimed to have prepared his zirconates. Ouvrard seems to have gotten little besides crystals of zirconia. Very little action could be seen in the experiments described below. The zirconia sank to the bottom of the fused mass, and remained without apparent change for hours. Varying the time of heating did not seem to have much effect upon the results.

After the fused mass had cooled it was leached with successive portions of water until no alkali could be detected. The wash water contained no zirconium. As the mass left will absorb carbon dioxide, it was dried as rapidly as possible at about 150° to constant weight. Dilute hydrochloric acid was used to separate the zirconate formed from the unchanged zirconia. As this zirconia was now in the ignited and even crystalline form,

* From the *Journal of the American Chemical Society*, xviii., No. 5.

it was concluded that it was insoluble in the dilute acid. The zirconia in the solution was precipitated as hydroxide and determined as oxide, and the alkali determined in the filtrate. Two grms. of zirconia were used in each case, and a large excess of the carbonate. The amount of unattacked zirconia ranged from 93 to 99 per cent, showing thus very little action after many hours of fusion. In some cases, therefore, the amount of supposed zirconate obtained was too small for reliable analysis.

A. With Sodium Carbonate.

Three experiments with sodium carbonate were carried to completion:—

1. Two grms. zirconia and 8 grms. sodium carbonate were fused three hours. Amount of residue after leaching, soluble in dilute hydrochloric acid, 0.1588 grm., or 8 per cent. In this $ZrO_2 = 75.70$ per cent; $Na_2O = 24.30$.
2. Two grms. zirconia fused with 16 grms. sodium carbonate for four hours. Amount of residue soluble in hydrochloric acid, 0.3042 grm. Percentages: ZrO_2 , 74.18; Na_2O , 25.81. These correspond fairly with $(ZrO_2)_3(Na_2O)_2$.
3. Two grms. zirconia fused with 16 grms. sodium carbonate for eight hours. Amount soluble in dilute hydrochloric acid, 0.1220 grm., or 6 per cent. Percentages: ZrO_2 , 58.16; Na_2O , 41.84.

B. With Potassium Carbonate.

When potassium carbonate was used the action was so slight that it was not possible to get enough for analysis. In one case, after heating for ten hours, the amount soluble was just one-half per cent. This accords with the observation of Ouvrard.

Of course it is possible that the leaching with water had a partially decomposing effect upon the zirconates. Very little could be justly concluded, however, from experiments in which there was so little action, therefore the effort at forming the zirconates by fusion with the carbonates was abandoned.

III. Fusion of Zirconia with Hydroxides.

1. *Fusion with Sodium Hydroxide.*—Here considerable action was noticed. The fusions were made in a silver dish. The heating was kept up until the mass became semi-solid. The treatment of the fused mass and the analysis were carried out as before. No zirconium was detected in the wash water.

1. Two grms. zirconia fused with 8 grms. sodium hydroxide. Total amount dissolved, 1.1855 grms. An analysis, reduced to dry basis, gave ZrO_2 , 92.29, and Na_2O , 7.65.
2. Same amount taken as in Experiment 1. Total amount dissolved, 0.7655 grm., containing ZrO_2 , 93.19, and Na_2O , 6.22.
3. Two grms. zirconia and 16 grms. sodium hydroxide. Amount dissolved, 0.8004 grm., containing ZrO_2 , 92.57, and Na_2O , 7.38.
4. Two grms. zirconia were fused with 8 grms. of sodium dioxide, instead of the hydroxide. Amount dissolved, 0.7074 grm., and this contained 91.21 per cent ZrO_2 .

$Na_2O.(ZrO_2)_6$ contains ZrO_2 , 92.20, and Na_2O , 7.80.

$Na_2O.(ZrO_2)_7$ contains ZrO_2 , 93.29, and Na_2O , 6.76.

2. *Fusion with Potassium Hydroxide.*—These were carried out in a manner similar to those with sodium hydroxide, and the action seemed to be about the same. In each experiment 2 grms. of zirconia were taken and fused with 16 grms. of potassium hydroxide.

1. Dissolved by hydrochloric acid 0.8850 grm., which contained 79.63 per cent ZrO_2 .
2. Dissolved 1.5241 grms., which contained ZrO_2 , 82.98; K_2O , 17.00.
3. Dissolved 1.2078 grms., which contained ZrO_2 , 78.59; K_2O , 21.40.
4. Dissolved 0.9297 grm., which contained ZrO_2 , 85.51; K_2O , 14.49.

In analysing these alkaline zirconates the water present was not determined. The moist powder was treated with hydrochloric acid, the insoluble portion caught upon a filter, and the zirconia and alkali determined in the filtrate and the results calculated upon a dry basis. If the analysis given by Hiortdahl is calculated upon a dry basis, it gives for ZrO_2 , 93.51, and Na_2O , 6.49, or very nearly the numbers gotten in Experiment 2 in the fusions with sodium hydroxide.

It is difficult to interpret the results of these fusions with the alkaline carbonates and hydroxides. The fusions do not yield the same definite results each time, and indeed it cannot be claimed from the analyses that definite zirconates have been prepared. Some allowance must be made for the imperfect method of separation of the zirconate from the unchanged zirconia, some of the former being taken up by prolonged digestion with hydrochloric acid. There is a marked tendency, however, toward the formation of certain zirconates under approximately the same conditions. Two of the experiments with sodium carbonate give results fairly in accordance with the formula $(Na_2O)_2(ZrO_2)_3$. In the fusion with sodium hydroxide the results range from $(Na_2O).(ZrO_2)_5$ [$ZrO_2 = 90.76$; $Na_2O = 9.24$], to $(Na_2O).(ZrO_2)_8$ [$ZrO_2 = 94.08$; $Na_2O = 5.92$], and it is with these that the analysis of Hiortdahl agrees, though his was a fusion with sodium carbonate. Why there should be this difference is not very clear. The tendency is manifestly toward the formation of what may be called the poly-zirconates, having a considerable excess of zirconic acid. In the case of potassium the carbonate failed to give a compound. The hydroxide gives results ranging from $(K_2O).(ZrO_2)_3$ [$ZrO_2 = 79.57$; $K_2O = 20.43$], to $(ZrO_2)_5(K_2O)$, [$ZrO_2 = 86.74$; $K_2O = 13.26$]; again polyzirconates with excess of zirconia.

Other fusions were carried out with sodium and potassium hydroxides, and the resulting masses were leached with dilute acetic acid, a solvent which had to be used in leaching away the alkaline earths in the subsequent experiments. In the case of sodium the leaching removed practically all of the alkali. In the case of potassium a substance containing ZrO_2 , 78.59 per cent, and K_2O , 21.41 per cent, was left. This nearly corresponds to the formula $K_2O.(ZrO_2)_3$. It is almost exactly the result gotten in one of the previous experiments.

3. Lithium gave no zirconate when the carbonate was used for the fusion. With the hydroxide it gave the following results:—

Two grms. ZrO_2 were fused with excess of lithium hydroxide, leached with dilute acetic acid and with water. This gave on analysis ZrO_2 , 89.11 per cent; Li_2O , 10.99 per cent. Percentage of ZrO_2 , calculated for $Li_2O.2ZrO_2$, is 89.13.

4. Calcium oxide was also heated for a number of hours with zirconia, and gave the following results:—

	I.	II.	Calculated for $CaO.ZrO_2$.
ZrO_2	70.11	70.83	68.54
CaO	29.88	29.14	31.46

These residues, after treatment with dilute acetic acid and water, were crystalline.

5. Barium hydroxide differs from that of calcium in that it fuses readily, and thus affords much better opportunity for reaction. The fusion gave abundant evidence of action. The excess of hydroxide was washed out with water. The carbonate present was dissolved away with dilute acetic acid until there was no more barium in the wash water. No zirconia was found in any of these washings. Towards the latter part of the washing the solid particles settled out with great difficulty. The residue was analysed with the following result:—

	Found.	Calculated for $BaO.ZrO_2$.
ZrO_2	55.51	55.95
BaO	44.49	44.05

This is a greyish white powder, very fine, and easily soluble in hydrochloric acid. Practically all of the zirconia was taken up, leaving little undissolved by the hydrochloric acid.

6. Strontium oxide was prepared by ignition of the nitrate, and heated in the same way as the calcium oxide. This mass was pinkish white, probably from slight impurities, and was completely soluble in dilute hydrochloric acid. On analysis the following results were obtained:—

	Found.	Calculated for SrO.ZrO ₂
ZrO ₂	54'22	54'55
SrO	45'77	45'45

7. The magnesia (8 grms.) and zirconia (2 grms.) were heated together for about four hours, and then treated in the same manner as the calcium fusion, *i. e.*, first leached with dilute acetic acid, and then washed with water until free from magnesia. The residue gave evidence of being crystalline:—

	Found.	Calculated for MgO.ZrO ₂
ZrO ₂	76'28	75'30
MgO.. ..	23'70	24'70

(To be continued).

CALCULATION OF THE CONDUCTIVITY OF MIXTURES OF ELECTROLYTES HAVING A COMMON ION.*

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(Concluded from p. 36).

Results of Observations on Mixtures.

(A).—Sodium and Potassium Chlorides.

THE following series of mixtures of potassium and sodium chloride solutions were examined:—

Concentration (Grm.-mols. per litre).		Conductivity, × 10 ⁸ .
KCl.	NaCl.	
3'88	5'12	2494
3'20	"	2326
2'49	"	2187
1'93	"	2029
3'88	5'12	2494
"	4'28	2404
"	3'37	2316
"	2'56	2196
"	2'06	2124
3'46	3'20	2160
3'80	2'23	1877

Table A contains a statement of the measured and calculated values of the conductivities of the above mixtures, with the concentrations of the constituent solutions, and the data necessary for the calculations, viz, the dilutions of the respective electrolytes and their ionic concentrations, in the mixtures, these data being obtained by Prof. MacGregor's graphical process. The measured values of the conductivity were obtained from the above observations by graphical interpolation.

The results of Bender's experiments, as calculated by Prof. MacGregor (*Trans. N. S. Inst. Sci.*, ix., p. 101), are given below for comparison.

Concentration (Grm.-mols. per litre).		Conductivity.		Difference, per cent.
KCl.	NaCl.	Measured.	Calc.	
2'0	2'0	1445	1458	+0'90
3'0	2'0	1823	1808'6	-0'79
2'0	3'0	1664	1660	-0'24
3'0	3'0	2007	1988'7	-0'91
2'0	4'0	1858	1849'3	-0'47
3'5	4'0	2303	2239'2	-2'77
4'0	4'0	2432	2345'3	-3'56

The two sets of observations agree very well together, the differences between calculated and observed values being of the same sign and in general for mixtures of about the same mean concentration of approximately the same magnitude.

The two series of mixtures of strong solutions show that the differences increase rapidly as the constituent solutions are more and more nearly saturated, reaching in the case of practically saturated solutions 6'4 per cent.

(B).—Sodium Chloride and Hydrochloric Acid.

The conductivities of the following series of mixtures of hydrochloric acid and sodium chloride solutions were measured:—

Constituent solutions. Concentration (Grm.-mols. per litre).		Conductivity of mixture, × 10 ⁸ .
NaCl.	HCl.	
2'02	4'55	4932
"	3'89	4492
"	3'29	4089
"	3'19	4073
"	3'06	3958
"	2'66	3623
"	2'56	3489
"	2'34	3323
1'04	4'55	5069
"	3'97	4682
"	3'80	4315
"	3'10	3989
"	2'86	3696
"	2'18	3112
"	2'11	3025
"	1'93	2824
"	1'58	2427
"	1'15	1928
0'607	1'120	1813
"	0'970	1620
"	0'815	1412
"	0'730	1296'5
"	0'603	1114
"	0'485	952

Table B contains in cols. 1 and 2 the concentrations of the solutions of hydrochloric acid and sodium chloride which were mixed, and in col. 7 the measured conductivities of the mixtures, obtained by graphical interpolation from the above observations. Cols. 3, 4, and 5 give the common concentration of ions and the respective dilutions of the electrolytes, in the mixture, as determined by Prof. MacGregor's graphical process. Col. 6 gives the calculated values of the conductivity, and the 8th the excesses of the calculated over the observed values expressed as percentages.

It will be seen that in the series of weakest solutions the differences between calculated and observed values are of such small magnitude and show such alternation of sign as to warrant the conclusion that they are due chiefly to accidental errors. In the two series of stronger solutions the differences are more irregular in magnitude and the alternation of sign is much less marked, the most of the differences being positive. The above results, therefore, seem to show that even in the case of two electro-

* *Transactions of the Nova Scotian Institute of Science*, vol. ix., Session 1895-96.

TABLE A.

Constituent solutions (Grm.-mols. per litre).		Dilution in the mixture.		Concentration of ions in the mixture.	Conductivity, $\times 10^8$.		Difference, per cent.
KCl.	NaCl.	KCl.	NaCl.		Calc.	Measured.	
3.75	5.12	0.247	0.143	2.013	2312	2469	-6.4
3.50	"	0.234	0.156	1.993	2276	2420	-6
3.00	"	0.205	0.1855	1.950	2202	2313	-4.8
2.50	"	0.175	0.216	1.890	2109	2190	-3.7
2.00	"	0.151	0.239	1.822	2013	2049	-1.7
3.88	5.00	0.26	0.14	2.014	2323	2481	-6.4
"	4.50	0.291	0.151	1.998	2295	2429	-5.5
"	4.00	0.335	0.166	1.980	2292	2377	-3.6
"	3.50	0.388	0.182	1.955	2261	2324	-2.7
"	3.00	0.462	0.205	1.916	2227	2260	-1.4
"	2.50	0.573	0.227	1.864	2174	2189	-0.7
"	2.00	0.750	0.250	1.788	2096	2116	-1.0
3.46	3.12	0.412	0.2295	1.848	2130.5	2160	-1.3
2.23	3.80	0.2432	0.2824	1.68	1875.5	1877	-0.08
2.87	4.69	0.225	0.202	1.924	2177	2222	-2

TABLE B.

Constituent solutions. Concentration (Grm.-mols. per litre).		Concentration of ions in the mixture.		Dilution in the mixture.		Conductivity of mixture, $\times 10^8$.		Differences, per cent.
HCl.	NaCl.			HCl.	NaCl.	Calc.	Measured.	
2	2.02	1.272	0.539	0.451		3020	3008	+0.4
2.5	"	1.392	0.592	0.398	"	3489.5	3456	+1.0
3.0	"	1.485	0.636	0.354	"	3885	3888	-0.08
3.5	"	1.570	0.668	0.322	"	4233.5	4260	-0.6
4.0	"	1.665	0.700	0.290	"	4622.3	4580	+1.0
4.5	"	1.740	0.726	0.264	"	4944	4880	+1.3
1	1.04	0.744	1.031	0.892		1751	1752	-0.005
1.5	"	0.916	1.215	0.708	"	2373	2332	+1.7 ⁶⁶
2.0	"	1.062	1.345	0.578	"	2928.3	2900	+0.9
2.5	"	1.196	1.431	0.492	"	3428.5	3398	+0.9
3.0	"	1.324	1.495	0.428	"	3906	3872	+0.9
3.5	"	1.440	1.555	0.378	"	4340.7	4316	+0.6
4.0	"	1.538	1.585	0.338	"	4715	4700	+0.3
4.5	"	1.628	1.616	0.307	"	5055	5036	+0.4
0.4	0.607	0.392	1.450	1.844		829.8	838	-1.0
0.5	"	0.436	1.636	1.656	"	983.4	976	+0.8
0.6	"	0.474	1.794	1.500	"	1125.5	1116	+0.8
0.7	"	0.508	1.922	1.372	"	1255	1250	+0.4
0.8	"	0.544	2.022	1.272	"	1384.7	1388	-0.2
0.9	"	0.582	2.121	1.173	"	1524.6	1525	-0.025
1.0	"	0.620	2.195	1.099	"	1658.6	1656	+0.16
1.1	"	0.655	2.267	1.027	"	1787.6	1784	+0.2
1.2	"	0.692	2.322	0.972	"	1917.1	1913	+0.2

lytes with a common ion, which differ so markedly in ionic velocity from one another as sodium chloride and hydrochloric acid, the dissociation theory enables us to calculate the conductivity of solutions containing both, within the limits of experimental error, up to a mean concentration of about 1 grm.-molecule per litre, and that in the case of solutions of greater mean concentration, the calculated value is greater than the observed.

Colorimetric Determination of Phosphoric Acid in Water.—Alessandria (*Pharm. Central Halle*).—The author uses the molybdenic mixture; and as a liquid for comparison, he takes a solution of 0.1 grm. calcium phosphate in a few drops of nitric acid, diluting first to 1 litre and then further. Silica must be previously eliminated. A high percentage of phosphoric acid is not objectionable from a sanitary point of view if derived from fossils, bones, &c.

HYDROFLUORIC ACID.*

By CARL F. STAHL.

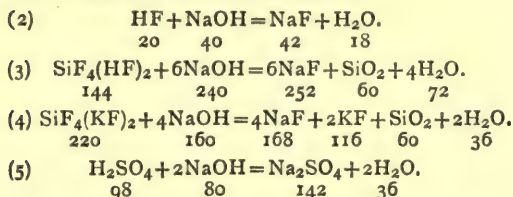
(Concluded from p. 37).

C.—Sulphuric Acid.

PLACE the platinum dish containing 4 grms. of the acid to be tested on a water-bath under a hood with a good draught and evaporate till acid fumes have completely ceased to be given off. Titrate the remaining syrupy liquid, which contains the free sulphuric acid, cold, with normal acid solution, using either litmus or phenolphthalein as indicator. The number of c.c. used we call "c."

* Abstracted from a Lecture before the Chemical Section of the Engineers Society of Western Pennsylvania, at Pittsburgh, February 28th, 1896. From the *Journal of the American Chemical Society*, xviii., No. 5.

The reactions involved are as follows:—



Now the number of c.c. of normal soda solution used in the first titration, and called "*a*," represents the alkali necessary to neutralise the hydrofluoric acid, hydrofluosilicic acid, and sulphuric acid, and in order to find the number of c.c. used for hydrofluoric acid alone, we have to subtract those used for hydrofluosilicic acid and sulphuric acid, but although we used the same weight (2 grms.) for the determination of the hydrofluosilicic acid, it would not be correct to subtract the number of c.c. used, because in the potassium silicofluoride two atoms of fluorine are neutralised, and we only neutralise with normal solution the remaining four atoms, which are combined with silicon. It would therefore have required—

$$b + \frac{b}{2} \text{ c.c.}$$

to neutralise the free acid.

Having employed 4 grms. of substance for the determination of the sulphuric acid, the number of c.c. used for that determination must be divided by 2. The number of c.c. used for hydrofluoric acid alone are therefore equal to—

$$a - \left(\frac{3}{2}b + \frac{c}{2} \right),$$

and as each c.c. normal solution indicates 0.020 gm. HF, and 2 grms. of substance have been used, the number of c.c. found by the above formula express, without further calculation, the percentage of free hydrofluoric acid. Therefore—

$$a - \left(\frac{3}{2}b + \frac{c}{2} \right) = \text{per cent free hydrofluoric acid.}$$

After the foregoing explanation, the calculation of the percentage of hydrofluoric acid is an easy matter. 1 c.c. normal sodium hydroxide indicates 0.055 gm. potassium silicofluoride, which was obtained from 0.036 fluosilicic acid; having used two grms. of substance, 0.036 has to be divided by 2 and multiplied by 100 to get the percentage, or—

$$b \times 1.8 = \text{per cent hydrofluosilicic acid.}$$

The percentage of free sulphuric acid is obtained by multiplying *c*, the number of c.c. used, by 0.048, dividing by 4, and multiplying by 100, or—

$$c \times 1.2 = \text{per cent free sulphuric acid.}$$

Other free acids, muriatic or nitric acid, which influence the accuracy of the determination, are not likely to occur in commercial hydrofluoric acid, and their presence can easily be detected by well-known analytical methods.

To give an idea of the composition of some of the makes of hydrofluoric acid I have appended a few of the analyses made in the course of five years:—

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Specific gravity ..	—	1.299	1.264	1.253	1.244	1.264	1.282	1.247	1.234
	P.c.	P.c.	P.c.	P.c.	P.c.	P.c.	P.c.	P.c.	P.c.
Hydrofluoric acid ..	39.6	42.2	44.3	48.1	48.6	51.1	54.2	48.6	33.5
Hydrofluosilicic acid	2.7	14.9	10.1	4.7	5.0	6.8	8.1	6.3	10.6
Free sulphuric acid ..	—	0.8	0.8	4.0	1.9	1.4	1.2	0.8	1.6

1. Oct., 1891. Baker and Adamson, C. P. acid in ceresine bottle, 0.005 per cent non-volatile residue.
2. Oct., 1891. Manufactured by J. C. Wiarda, sample received.

3. Nov., 1891. Manufactured by J. C. Wiarda, sample taken from package of 100 lbs.
4. Jan., 1892. Manufactured by James Irwin and Co., sample of lot of 3500 lbs.
5. Mar., 1892. Manufactured by James Irwin and Co., sample of lot of 3400 lbs.
6. Jan., 1894. Manufactured by Bender and Aldred, sample taken from package of 100 lbs.
7. Jan., 1895. Manufactured by James Irwin and Co., sample taken from tank holding 3000 lbs.
8. Oct., 1895. Manufactured by James Irwin and Co., sample taken from tank holding 3200 lbs., 0.015 per cent non-volatile residue.
9. Jan., 1896. So-called "pickling acid," sample received from a foundry.

By comparing analyses Nos. 2 and 7, it can be seen what influence hydrofluosilicic acid has in raising the specific gravity; although No. 2 has a higher specific gravity than No. 7, it contains 12 per cent less hydrofluoric acid, but 6.8 per cent more hydrofluosilicic acid. Nos. 3 and 6 have the same specific gravity, but No. 6 contains 6.3 per cent more hydrofluoric acid, and 3.8 per cent less hydrofluosilicic acid. The influence of sulphuric acid on the specific gravity can be seen by comparing Nos. 4 and 5.

A great difficulty in the manufacture of hydrofluoric acid is the very disagreeable and dangerous nature of the gaseous and liquid acid. The effects of the fumes on the respiratory organs are more injurious than those of other acids. Still more marked are the effects of the liquid acid on the skin. One drop of acid, although it does not make itself felt for a few hours, will, even on the horny skin of a workman's hand, cause a very painful inflammation in one-half day. Against the fumes the workmen protect themselves by respirators, or by the simpler way, which they usually prefer, of tying a handkerchief over nose and mouth and by greasing the unprotected parts of the face with lanolin. The latter is as effective as vaseline and easier to wash off. Against liquid acid rubber gloves afford protection. If liquid acid comes in contact with the skin it should be washed off at once with water and aqua ammonia, or another alkali, which will prevent injury.

In conclusion, I wish to say a few words about the different applications of commercial hydrofluoric acid.

The oldest, and up to the present time most extensive, application is for etching glass. For this purpose it can be applied in three different ways. In the gaseous form by suspending the articles to be etched over a mixture of fluor-spar and sulphuric acid. This is the oldest way of etching, and I believe most burettes, graduated cylinders, &c., for laboratory use are still marked in this way. If applied in gaseous form the acid leaves the surface opaque, while the liquid acid leaves the surface smooth and transparent. For the production of an opaque surface with liquid acid many empirical formulæ are published, and every glass factory, or rather every etching boss, has his own secret formula. But they all aim to produce a mixture of hydrofluoric acid with a fluoride of ammonium, or potassium, or sodium, with which a number of other substances, such as sulphuric, acetic, or muriatic acids, or ammonium or potassium sulphate, &c., are mixed, but it seems quite unnecessarily. Hydrofluoric acid prepared for etching opaque, goes under the trade name of "white acid." Lead glass is very rapidly and uniformly etched, and acid of 45 to 48 per cent is usually employed, while lime glass requires a stronger acid and more time. Lately, acid as strong as 52 per cent HF is employed. "White acid" is much more convenient for application than gaseous acid, and acts very rapidly; for instance, a lead glass lamp chimney can be rendered opaque by simply dipping it into the acid for one minute. Lime glass, even with acid specially prepared for it, requires about two minutes immersion. It is important that the temperature of the acid and the glass should be about 15°

C. Parts of the glass which are to remain unetched, must be protected. For this purpose a number of substances are in use. Asphaltum varnish is usually employed, when the design is printed on paper and then transferred to the glass; for the so-called needle-work, a mixture of Burgundy pitch and bees'-wax is used.

A more recent application of hydrofluoric acid is for cleaning castings from sand. These have so far been cleaned, either by mechanical means or with sulphuric acid; but the first is expensive, and neither way, in many cases, satisfactory. The sulphuric acid loosens the sand by dissolving the iron to which it is attached, while hydrofluoric acid dissolves the sand itself and therefore acts more promptly and does not cause any loss of iron. It also dissolves the magnetic oxide formed on the surface of the iron very readily, much more so than sulphuric acid. This latter point is important for castings which have to be worked afterwards with edged tools, the magnetic oxide being very hard. For cleaning castings, the acid is diluted to about 1 or 2 per cent HF; the pickling can therefore be carried on in wooden vessels.

Some of the firms who use hydrofluoric acid for cleaning iron have kindly sent me reports on it. The most interesting parts of these reports I will mention here with their permission:—

Mr. S. H. Stupakoff, Supt. Union Switch and Signal Co., writes:—

"We use the acid in the proportion of 2½ quarts to one-half barrel water, containing about 25 gallons,"—equal to one pound 48 per cent hydrofluoric acid in 35 pounds of water, the liquid would therefore contain 1.4 per cent HF—"the bath is filled to the top with castings and they are left in it for about half an hour. We can renew our charge by adding each time one quart of acid.

"We find that the hydrofluoric acid is vastly superior to sulphuric acid, as the latter will not pickle satisfactorily in less than one day, and besides this we use about double the quantity of sulphuric acid compared with hydrofluoric acid to pickle the same amount of castings." (As the quantities given by Mr. Stupakoff are by volume, this would be equal to one pound of 93 per cent sulphuric acid in 11 pounds of water; the liquid would therefore contain 8½ per cent sulphuric acid, or six times as much as the hydrofluoric acid bath).

"With the sulphuric acid we experienced a great deal of trouble by obtaining a white sediment on the castings, which was very difficult to remove, even when washed in hot water. This white coating would frequently work through the paint with which the castings were subsequently covered."

"We had no occasion to try this acid for cleaning any other material but cast-iron, with the exception of one instance, when we tried to remove heavy coatings of rust from a lot of mixed material, consisting of cast-iron and wrought iron. The hydrofluoric acid did this to perfection, and left a perfectly bright surface.

"I can say, in conclusion, that I am perfectly satisfied that the use of hydrofluoric acid for the cleaning of new castings and corroded iron is certainly a success, and I will always prefer it to the old method of pickling in sulphuric acid."

From the engineer of another firm I received the following report:—

"The best solution is 1 to 30." (This is by volume, and the bath would contain, as he used 48 per cent hydrofluoric acid, about 2 per cent HF). "As we make no small castings of grey iron, I have only used the acid on malleable castings, with the result that small castings are cleaned excellently in two hours. I have also cleaned castings in a mixture of 1 acid to 50 water"—the bath would contain about 1 per cent HF—"by leaving them in over night, but we prefer to clean with the stronger acid. The pickling vat is usually filled up with castings three times before it requires more acid.

"It takes sulphuric acid twice as long with the same proportion"—that is, 1 to 30 would give a solution of

about 5½ per cent sulphuric acid—"and then does not eat into the corners as well as hydrofluoric acid; also wastes more iron, and does not leave it bright."

For iron which is to be enamelled, the cleaning with hydrofluoric acid is also advantageous, because it leaves a purer metallic surface than can be obtained with other acids.

I am informed that a large firm in this city is at present making arrangements with a view of throwing out their whole mechanical cleaning plant, in which they have been cleaning 60 tons a day.

Hydrofluoric acid or its salts is also used in distilleries to insure a more complete fermentation (Dr. Leo Backeland, *Journ. Am. Chem. Soc.*, xiv., 212).

The latest application, of which I heard only a few days ago, is for cleaning out oil and gas wells. It seems that the shooting of a well sometimes packs the rock so tightly that the hole is drier after the shooting than before. By pouring about six barrels of hydrofluoric acid (I suppose the acid is used diluted) into the hole, which dissolves the silicates and afterwards is pumped out again, gas or oil get an outlet.

NOTICES OF BOOKS.

Painters' Colours, Oils, and Varnishes: a Practical Manual. By GEORGE H. HURST, F.C.S., Member of the Society of Chemical Industry; Lecturer on the Technology of Painters' Colours, Oils, and Varnishes at the Municipal Technical School, Manchester. Second Edition, Revised and Enlarged. With numerous Illustrations. London: Charles Griffin and Co., Ltd. (All rights reserved). Pp. 499.

MR. HURST has now fairly acquired recognition as an authority on the important class of compounds described in this work. He seems to use "assay" as synonymous with qualitative examinations, and in contradistinction to "analysis."

Among the white pigments we find China clay, the principal use of which is not as a pigment, but as a means of giving a specious body to calico. If introduced in aniline lakes for paper-staining and tissue-printing, its freedom from grit is a vital point.

Many substances are here described as substitutes for white lead, but, in spite of persevering efforts, that prospect of the displacement of that unsanitary body does not seem very near at hand. The "white leads" of Wilkinson and Pattinson have gone out of use.

Among red pigments a brief notice is given to mercuric iodide, HgI₂. This compound is often known as "brilliant scarlet" and as "geranium red." It is more permanent when obtained by grinding mercury and iodine together in proper proportions than when prepared by precipitation.

Pink colour, or stannic chromate, is not mentioned at all, though, according to the observations of Gentele and our own, it perfectly resists all external agencies.

In speaking of the chromes Mr. Hurst mentions the vicious custom of the trade calling pigments contaminated with lead sulphate "pure chrome," whilst common chromes contain barium sulphate, or any other cheap white base, in addition.

Chrome-red is remarkably rich in synonyms. Among these we find "Persian red,"—an *alias* of pink colour.

Among the ochres and sienna the Oxfordshire ochre is recognised as excelling all other ochres, both in brightness and covering power. The American ochres are described as being, for the most part, ochres in name only; one sample analysed by the author was found to contain 75 per cent of barium sulphate.

The "Mars colours" of the late George Field are described as having no advantage over ochres and iron

reds as regards brightness and permanence of tone, but as being more expensive.

Turner's yellow and Naples yellow have been greatly, if not entirely, superseded by the chromes. Turner's yellow was at one time known as Montpellier yellow, Kassel yellow, Verona yellow, and mineral yellow.

King's yellow, an arsenical colour, As_2S_3 , is fortunately in much less repute than it was formerly.

The Brunswick greens now made are, in fact, mixtures of Prussian blue and of chrome-yellow, whilst the old Brunswick green is—or rather was—a basic copper chloride. It was too expensive, owing to the tediousness of its preparation.

True chrome-greens, such as that of Guignet, are strongly recommended, and are carefully distinguished from the mixtures of Prussian blue and chrome-yellow often sold under the same name. The insolubility of Guignet's green renders it perfectly unobjectionable from a sanitary point of view.

Emerald-green is a beautiful colour, but as an arsenical compound it affects the health of persons making it or using it, in a most capricious manner, depending on physiological idiosyncrasy. If exposed to damp air it undergoes gradual decomposition.

Cobalt green (Rinman's green) is in little demand on account of its high price. The author points out that, should a cheap source of cobalt be discovered, it might come into extensive use.

Ceruleum, the old Egyptian blue colour, is at present an unsolved riddle as to the method of its preparation, unless the recent announcement by a French chemist should be verified.

Carmine is mentioned as the best type of a lake colour. Its composition is not by any means thoroughly known. The receipt of Madame Cenette, of Amsterdam, is defective. The author, like ourselves, has not succeeded in preparing a satisfactory carmine according to its direction.

Under the head of "Varnish-making" we learn that amber is found in the Hukong Valley, in North Burmah, at an elevation of 1050 feet above the sea-level, and is regularly mined for. The account given of the gums, or rather resins, used in varnish making, is very elaborate.

We do not think that there can be found in our scientific and technical literature any work which can compete with that of Mr. Hurst.

Ammonia: the New Procedures for its Manufacture and its Applications. ("L'Ammoniaque: ses Nouveaux Procédés de Fabrication et ses Applications"). By P. TRUCHOT. Paris: Bernard Tignol.

This valuable monograph forms No. 64 of the "Bibliothèque des Actualités Industrielles," and is a work of most unquestionable merit. The demands for ammonia have multiplied and extended to such an extent that the search for new and improved sources of this necessary compound has been intensified throughout the civilised world. No longer can we content ourselves with the destructive distillation of animal matter, such as camel's dung or horns and bones. Every chemical process in which nitrogen is thrown off in combination with hydrogen is made to contribute its quota. Yet so great is our need for ammonia, that further supplies are still called for. Almost incalculable wealth is awaiting the inventor who can prevail upon the free nitrogen of the atmosphere to combine with hydrogen on a large scale, but hitherto "the haughty demon mocks our spell."

M. Truchot commences his task with physical considerations bearing upon the manufacture of ammonia, such as the specific gravities of ammonia and its salts, their melting- and boiling-points, indices of refraction, specific heats, solubilities in water and alcohol, vapour-tensions, densities, and boiling-points of saturated solutions, thermo-chemical data, refrigerating mixtures, and

a comparison of the various hydrometric standards. It is scarcely needful to say that the author clings to Baumé despite its inconveniences.

The second chapter gives us the history of ammonia from Pliny, Dioscorides, and Ramon Lull.

In the third chapter follow the chemical and physical properties of ammonia and of the ammonium salts, their behaviour with heat, with electricity, with oxygen and platinum sponge, with the halogens, sulphur and boron; and the modes of formation of ammonia.

In the fourth chapter we pass to the manufacture of ammonia from natural products, from atmospheric nitrogen, from coal, from nitrate of soda, from nitrogenous organic matters, from urine, sewage, excrements, vegetable dregs, and peat.

Coal is rightly described as constituting at present the main source of ammonia, whether as a by-product of the gas manufacture, or in coke burning, or in the working of blast-furnaces.

It is estimated that if all coke-ovens were fitted for the condensation of the by-products, we should have from this source a yearly yield of 273,000 tons sulphate of ammonia, the chief part of which is still going to waste. The number of coke ovens properly fitted for this purpose in Britain is only 413, whilst in Germany more than 1250 are in action; though we manufacture about double the quantity of coke.

Mr. Mond, calculating the amount of fuel burnt yearly in Britain at 150,000,000 tons, estimates that if only one-tenth of this quantity were treated by his process our annual production of sulphate of ammonia would reach the enormous figure of five million tons!

The synthetic production of ammonia is most carefully and thoroughly considered. Nitrogen and hydrogen have been made to combine by various experimentalists, but the processes unfortunately are not remunerative.

In spite of numerous assertions and varied researches, the reactions attempted have never proved practical, or at least not capable of industrial success. The intervention of boron and titanium has not been remunerative.

It is, of course, demonstrated that certain vegetables, by virtue of lower plants which are attached like tubercles to their roots, are able to supply themselves with synthetic ammonia, and can thus dispense with nitrogenous manures. For the details of this most important subject the reader is referred to the lectures of Georges Ville, translated by W. Crookes, F.R.S. (Longmans).

M. Truchot's work includes instructions for the analysis of ammonia and its salts, of nitrogenous substances, and of ammonia in waters and in crude coal-gas.

The applications of ammonia and of the ammoniacal salts are treated at some length, and there is a summary of the principal patents concerning the compounds, and a brief bibliography.

The work deserves very emphatic recommendation.

Influence of Trees on Malaria.—A medical contemporary mentions, on the authority of Dr. Alexander, Medical Officer of Health for Poplar and Bromley, that the planting of osiers on a large scale in North-western India has been useful in stamping out malaria in a notoriously unhealthy valley covered with stagnant pools. Sanitarians will do well to bear this fact in mind.

Detection of Dulcin in Beverages.—Morpurge (*Pharm. Central Halle*) evaporates the liquids with 1-20th part of lead carbonate, and extracts repeatedly with alcohol. From the dry residue of the united alcoholic extracts approximately pure dulcin can be extracted with ether. The liquid is heated for a short time with 2 drops of phenol and 2 drops of concentrated sulphuric acid; the syrup thus formed is diluted with a few c.c. of water, and the solution is superstratified in a test-tube with a little ammonia. If dulcin is present, the surface of contact of the two liquids takes a blue or violet colour.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 26, June 29, 1896.

M. Albert Gaudry announced to the Academy the death of Sir Joseph Prestwich, a correspondent of the Academy in the Geological Section.

The Academy proceeded to nominate a correspondent for the section of Astronomy, *vice* Prof. Newcomb, who has been elected a Foreign Associate. M. Backhuysen was elected by a large majority.

Spectrum of Phosphorus in Fused Salts, and in certain Metallurgical Products.—A. de Gramont.—(See p. 41).

On Blue Nitrosodisulphonic Acid, and on some of its Salts.—Paul Sabatier.—This acid has the composition $\text{NO}(\text{SO}_3\text{H})_2$. The sulphuric solutions of the free acid are gradually decomposed at ordinary temperatures into sulphuric acid, sulphurous anhydride, and nitric oxide. This decomposition is not very rapid at 100° . If agitated with air, the solutions are quickly decomposed by oxidation, giving off nitrous vapours and forming nitrosulphuric acid. A solution of hydrogen peroxide in concentrated sulphuric acid effects a rapid decolouration. Chlorine produces an analogous result, but bromine acts much less rapidly, and remains for some time as a greenish solution. Iodine used in a sulphuric acid solution has scarcely any action. Water destroys the compound, with the production of nitrous gas and sulphuric acid. The addition to the blue liquid of most metallic oxides, anhydrous or hydrated, and also of carbonates, generally brings on a violent action, which leads to the destruction of the blue acid and the exclusive production of sulphates. This takes place with the alkaline and alkaline-earthly oxides or carbonates; those of nickel, cobalt, magnesium, aluminium, silver, lead, cadmium, and zinc. Ferric acid introduced into the refrigerated blue liquid at about 0° gradually dissolves without any escape of gas, yielding a vinous-rose liquid. Green cupric carbonate gives a deep blue solution, with an escape of carbonic gas; the solution is rather more violet than the acid which has produced it, and of an incomparably more intense shade. A bright iron nail plunged into the nitrososulphuric solution is immediately covered with a very brilliant rose tint, and there soon appear rose-coloured threads setting out from the metal and diffusing themselves in the liquor, which they colour of a rose-cobalt shade, more and more intense. This is a fine lecture experiment.

Action of Iodine upon Stannous Chloride.—V. Thomas.—The author expected that stannous chloride must be capable of fixing iodine so as to give rise to an addition chloro-iodide, SnCl_2I_2 . Anhydrous stannous chloride, finely powdered, was placed in a perfectly dry flask; upon the stannous chloride there was introduced carbon disulphide holding iodine in solution. This was at first rapidly decolourised, then by degrees the violet-red tint of the iodine gave place to a pale yellow tint, which grew gradually deeper, and soon became a reddish orange. It results from the author's experiments that tin chloro-iodide cannot be obtained in this manner.

New Method for the Preparation of Aromatic Aldehyds.—L. Bouveault.—In former papers the author has given an account of the attempts which he has already made to convert the glyoxylic acids of the aromatic series into aldehyds. He has now found that this transformation can be effected in a quantitative manner by means of aniline.

Thermic Researches on Uranium Compounds.—J. Aloy.—The author has studied the solution-heats of the principal soluble salts of uranyl, and the formation-heats of the dissolved salts of uranyl.

Researches on the Chloridation of Gallic Acid. Formation of Dichlorogallic Acid and of Trichloropyrogallol.—Alexander Biétrix.—The products of the chloro-substitution of gallic acid have not yet been prepared. On passing a current of chlorine into an aqueous solution of gallic acid, we remark the appearance of a black colour, which disappears on the prolonged action of the chlorine. The author examines the stages of this transformation.

Crystallographic Properties of Benzylidene, Methyl- and Ethylsalicidenes, and Anisol Camphors.—J. Minguin.—This memoir is not well suited for abstraction.

Isanic Acid: a New Non-saturated Fatty Acid.—Alex. Hébert.—The Isano seeds from the Loango country, known also as Ungueko, are derived from a large tree of the family of Olacineæ. In the oil the author has recognised three fatty acids:—1. A liquid yellow acid, which we have named oleic acid, and which forms about 15 per cent of the total acids. 2. A liquid acid, brown and highly oxidisable; its properties are those of linoleic acid, and its proportion is about 75 per cent. 3. A white solid acid, present in the proportion of about 10 per cent. This acid is present in fine leafy crystals, fusible at 41° , very soluble in strong alcohol, ether, chloroform, benzene, acetone, methylic alcohol, and petroleum ether. Its composition is $\text{C}_{14}\text{H}_{20}\text{O}_2$.

Zeitschrift für Analytische Chemie.
Vol. xxxv., Part 1.

Detection of Saccharin in presence of Salicylic Acid.—Hr. Hairs (*Pharm. Central Halle*).—The author eliminates the salicylic acid as bromosalicylic acid. The liquid is then acidulated with hydrochloric acid and mixed with a moderate excess of bromine water. The bromosalicylic acid is filtered off, freed from excess of bromine by a current of air, and extracted with ether.

Determination of Halogens in Organic Substances.—J. Walker and J. Henderson (*CHEM. NEWS*).

Determination of Alkyl combined with Nitrogen.—J. Herzig and H. Meyer (*Monatshefte für Chemie*).

Determination of Formic Acid.—A. Lieben titrates with permanganate in a solution rendered alkaline with soda. (See *American Chemical Journal*, xvii., No. 7.)

Determination of Milk-Sugar.—G. Denigès (*Journ. de Pharm.*).—The colour of cow's milk is yellowish, and of goat's milk pure white.

Zinc in American Apple-Rings.—R. Hefelmann (*Pharm. Central Halle*).—Is probably due to the international addition of zinc-salts. (To what end?)

Preservation of "Hack-flesh" (*Forsch. Berichte über Lebensmittel*).—H. Kämmerer.—For the preservation of this disgusting substance, sodium sulphite or the corresponding bisulphite is added.

Examination of Caviare.—Niebel (*Zeit. für Fleisch und Milk Hygiene*).—According to the author, caviare should be neutral to litmus and contain neither free ammonia nor hydrogen sulphide.

Detection of Mineral Acids in Presence of Organic Acids, especially in Vinegar.—Niokol (*Pharm. Zeitung*) uses the well-known violet colour of lignin by mineral acids with phloroglucine. The vinegar is mixed with phloroglucine, and a splinter of pine-wood or a fragment of bamboo is boiled in the liquid for some time.

Microchemical Determination of Starch and Ethereal Oils in Adulterated Cloves.—H. Krämer (*American Pharm. Association*).

Determination of Sugar.—R. Farnsteiner (*Forschungsberichte über Lebensmittel*, ii., 235).

Volumetric Determination of Sugar.—Zdenek Peska. —The author recommends the modification of Fehling's solution, proposed by Pavy. (See CHEMICAL NEWS, lxxi., p. 235).

Determination of Thiophen in Benzene.—(From *Comptes Rendus*, cx., p. 781).

Determination of Anthracen.—H. Bassett (CHEM. NEWS, lxxi., p. 202).

The Chemical Laboratory of the Brewer.—W. Windisch. —A highly commendatory notice of a special work.

Analysis of Fats, Oils, and Waxes.—Hr. Benedikt. —English version by J. Lewkovitsch (Macmillan).

Examination of Water.—H. Nordlinger (*Pharm. Central Halle*). —In order to detect the possible entrance of cesspool liquids into wells, the author makes use of saprol. Cresoliferous disinfectants can be detected by smell at the dilution of 1 : 1,000,000, and by the characteristic taste if diluted to 1 : 2,000,000.

Distinction between Ground Rice and Buckwheat.—A Lehn and Hansek. —The latter authority finds a microscopic comparison sufficient.

Determination of Fats in Foods without previous Desiccation.—Hr. Hefelmann (*Pharm. Central Halle*) uses Werner Schmid's method for the determination of milk fat (*Zeit. Analyt. Chemie*, xxvii., p. 464).

Ash in Commercial Milk-sugar.—Braithwaite (*Pharm. Central Halle*). —In pure sorts the ash should not exceed 0.25 per cent.

Examination of Milk.—Notices of the determination of the specific gravity of coagulated milk by Mats Weibull (*Pharm. Central Halle*); determination of solids and fats in milk, by H. Weller (*Forschungs-berichte über Lebensmittel*); determination of albumenoids in milk, Gruber (*Zeit. f. Nahrungsmittel Untersuchung*), multiplies the total nitrogen by 6.37, instead of 6.5. Against this proposal Meissl objects.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Electrolytic Separation of Copper.—Can you give in your much esteemed paper a method for the electrolysis of copper bullion containing arsenic, antimony, gold, and silver; that is, how to keep the four metals mentioned in solution while the copper precipitates. Also, can you give a method for the determination of As and Sb in copper bullion, where these metals are present in quantities less than one-tenth of 1 per cent.—C. S. RICHARDSON.

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1914.

COAL-DUST.

THE QUESTION OF PRIORITY.

By W. GALLOWAY.

IN the report of a lecture given *in extenso* at page 64, *et seq.*, in the *Colliery Guardian*, of the 10th inst., on "Coal-dust and Explosives, by Mr. H. Richardson Hewitt, of Derby, H.M. Inspector of Mines, the following remarkable statements occur:—

"It was but a few years ago that the Messrs. Atkinson first drew attention to their idea that coal-dust was a dangerous element in mines where blasting operations were carried on."

"After Messrs. Atkinson first drew attention to the subject Professor Galloway took it up and made some rough experiments by placing gunpowder cartridges in heaps of coal-dust and firing them in the dark."

Although these statements were obviously uttered in ignorance of the nature of my experiments, they raise a distinct and palpable issue as to priority.

The facts are as follow:—

My first experiments with coal-dust were made on the 3rd of July, 1875. I then discovered that a mixture of air and fire-damp which is not inflammable at ordinary pressure and temperature, on account of the smallness of the proportion of fire-damp present in it, becomes inflammable when coal-dust is added to it, and can be ignited by means of a comparatively small flame.

On the 22nd of December, 1875, I gave evidence in the capacity of Assistant Inspector of Mines at the Coroner's inquest on the Llan Colliery explosion (South Wales District), when I attributed that explosion principally to the influence of coal-dust. My evidence was discountenanced by the Chief Inspector of Mines for the district, and was not embodied in the Reports of the Inspectors of Mines, but it was reported *verbatim* in the two local newspapers (*Western Mail* and *South Wales Daily News*) of 23rd December, 1875.

On the 2nd of March, 1876, I read my first paper, entitled "On the Influence of Coal-dust in Colliery Explosions," before the Royal Society. In that paper I announced the coal-dust theory.

In 1878 I published a large number of articles in *Iron* under the title of "Coal-dust Explosions." In these articles, amongst many other things, I quoted and commented upon what Faraday and Lyell had written about coal-dust upwards of twenty years previously, and I gave complete translations of the papers that had been published in France having a bearing upon the subject.

Besides contributing a number of other articles and papers on the same subject to various societies and periodicals, I read altogether five papers "On the Influence of Coal-dust in Colliery Explosions" before the Royal Society, viz., 2nd March, 1876, already referred to; 27th February, 1879; 30th May, 1881; 29th December, 1881; 8th May, 1884; and one on "A Coal-dust Explosion," 17th February, 1887.

During the ten years ending in 1885 I was engaged from time to time in carrying out experiments with coal-dust; first, with apparatus provided by the Glamorgan Coal Company, Limited, and erected at their Llwynypia Colliery; secondly, with apparatus purchased by means of Government grants obtained through the Royal Society; and, thirdly, with apparatus belonging to the Royal Commission on Accidents in Mines.

Before the accounts of my earlier investigations, and the conclusions founded upon them had appeared, the Inspectors of Mines and other mining experts were practically unanimous in attributing the cause of every great colliery explosion to the sudden outburst of a large volume of fire-damp which was supposed to have flooded the workings, become mixed with the air, and on being ignited in one way or another, produced the various phenomena subsequently observed. This explanation was accepted everywhere as the only one possible; it was recorded in the official reports of the Inspectors of Mines, and they, as well as the experts of that generation, were irretrievably committed to it.

There was not, figuratively speaking, a ripple of dissent from this mode of explanation upon the placid surface of mining opinion at the moment the coal-dust theory was launched upon it.

At first the new theory was ignored; then it was scouted; then it was subjected to scathing criticism; then it was taken up in a tentative manner by some of the younger and bolder men; and, lastly, when it was found to be making serious headway, one of the more adventurous spirits suddenly discovered that it was not new after all, for had not Faraday and Lyell and certain French engineers been its real authors?

Following my lead, first a joint paper by Messrs. Hall and Clarke was contributed to the North of England Institute, in May, 1876, then another by Messrs. Marreco and Morrison, in 1878, all of whom, with the exception of Mr. Clark, had previously corresponded with me on the subject of explosions; finally, in the year 1879, after the publication of my articles on "Coal-dust Explosions" in *Iron*, and during the next few years afterwards, a very great army of investigators, headed by Government Commissions in England, France, Prussia, and Saxony, and including the Messrs. Atkinson, entered the field.

Some of these investigators contented themselves with criticism pure and simple; others, of whom many had neither aptitude nor training for the work, made experiments with small and imperfect apparatus, and, as a consequence, obtained only negative results; still others were carried away by the side issues; and only a few, such as the Prussian and Austrian Commissions, and Messrs. Hall and Atkinson, H.M. Inspectors of Mines, did really good and substantial work of an enduring kind.

The facts and conclusions recorded in my earlier papers were freely drawn upon; by some they were generously acknowledged; by others they were first denounced and then assimilated; by others they were adopted without acknowledgment; while some of my experiments, and notably my investigation into the nature of the fire-damp cap (*Proc. Roy. Soc.*, 2nd March, 1876), were repeated with some variations and described as if they were original.

A flood of literature was now poured upon the mining world from every side, embodying opinions of the most conflicting and mystifying character, such as a mixture of coal-dust and air may take fire but it cannot explode; coal-dust can only carry flame from one accumulation of fire-damp to another; a coal-dust flame cannot extend throughout the workings of a mine in the entire absence of fire-damp; a small proportion of fire-damp must always be present in the air when an explosion takes place; some kinds of coal-dust are more inflammable than others; and so on—so that amid the din and hurly-burly of the strife the main question of how to put an end to great explosions was almost lost sight of.

But the scene of each successive explosion when viewed under the new light served gradually to dispel the Will-o'-the-Wisps which the majority of the investigators had been following pertinaciously for years; and thus it has come to pass that the new generation of Inspectors of Mines, and those who have been associated with them in investigating the phenomena of explosions, have become convinced, I believe almost to a man, of the soundness of the coal-dust theory; and that the struggle of contending

factions, which was at its height ten or twelve years ago, has gradually subsided, leaving us face to face with a work which still remains to be done, namely, to render the occurrence of a great colliery explosion impossible in the future.

Into the consideration of that problem I do not propose to enter on the present occasion, as I have lately done so in considerable detail in the pages of the *Daily Chronicle* of 24th June of the present year.

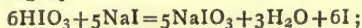
Cardiff, 17th July, 1896.

A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF THE SOLUBLE COMPOUNDS OF IODINE.

By Professor Dr. E. RIEGLER.

THE principle of the method is liberation of iodine in the iodides by iodic acid (HIO_3), solution in petroleum ether, determination of the excess of iodic acid by titration with a decinormal solution of sodium thiosulphate, and, from the quantity of iodic acid consumed, calculating the quantity of iodine corresponding to the iodide.

If a solution of iodic acid is brought in contact with the solution of an iodide, iodine is separated according to the following equation:—

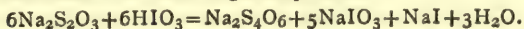


that is, to each atom of iodine liberated there belong $\frac{1}{6}$ th atom of the iodide.

Now, as according to the above equation an atom of iodine corresponds to a mol. of iodic acid, it is evident that, instead of the iodine, we may determine the quantity of iodic acid consumed for liberating the iodine from the iodide.

The solution of iodic acid which I employ for this purpose is decinormal, and it is prepared by dissolving 17.6 grms. iodic acid (HIO_3) in 1 litre of distilled water. In preparing the decinormal solution of thiosulphate, we proceed from the decinormal solution of iodic acid.

If a solution of thiosulphate mixed with a solution of starch is brought in contact with a solution of iodic acid, there ensues the following transposition:—



Consequently, as long as an excess of thiosulphate is present in the liquid, the starch is not coloured blue by the gradual addition of the solution of iodic acid; but in the moment when the first drop of this acid is added in excess, the iodine is liberated and colours the starch blue, which consequently acts as an indicator.

As it follows from the above equation, a mol. of sodium thiosulphate corresponds to each mol. of iodic acid, therefore 1.10th mol. of sodium thiosulphate corresponds to 1 litre decinormal solution of iodic acid,—i.e., 17.6 grms. iodic acid correspond to 24.8 grms. crystallised sodium thiosulphate.

We weigh therefore about 28 grms. crystalline thiosulphate, dissolve it in a litre of water, test the solution with the decinormal solution of iodic acid, and dilute accordingly.

By means of these two decinormal solutions we determine in the following manner the iodine in the iodides under examination:—

Into a parting funnel with a ground glass stopper we introduce a known number of c.c. of the iodide solution (which must not be more concentrated than 1 per cent), add from a burette an equal number of c.c. of the decinormal solution of iodic acid, shake well up, add 20 c.c. of petroleum ether, into which the greater part of the liberated iodine passes after vigorous agitation; after about a quarter of an hour the liquid below the stratum of petroleum ether is allowed to run into a beaker by opening the glass cock. The solution of petroleum ether

is poured away out of the parting funnel, into which the liquid from the beaker is again introduced with about 15 c.c. of pure petroleum ether, which after vigorous shaking will take up the last residues from the liquid. The aqueous solution is now passed from the parting funnel into a small flask by opening the glass cock, and, after the addition of a little starch solution, the excess of iodic acid is titrated back by means of the decinormal thiosulphate solution. The number of c.c. of decinormal thiosulphate solution which show the excess of iodic acid are deducted from that of the decinormal iodic acid solution employed. The difference thus obtained, multiplied by the factor $0.0127 \times \frac{1}{2} = 0.00635$, gives as product the quantity of iodine corresponding to the decomposed iodide.

If the quantity of iodine found in this manner is multiplied by the factor 1.368, we find it expressed as potassium iodide; if multiplied by 1.1811, we obtain it as sodium iodide.—*Zeit. Analyt. Chemie*, xxxv., p. 305.

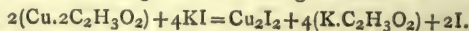
THE COPPER ASSAY BY THE IODIDE METHOD.

By ALBERT H. LOW.

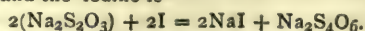
THE last edition of Dr. Peters's "Modern Copper Smelting" contains a description of the writer's modification of the copper assay by the iodide method. The following description of the same method embodies whatever changes have been deemed desirable up to date, as the result of almost daily work upon copper ores and products. For the most accurate technical work I prefer it to all other methods. For practical work it exceeds the electrolytic method in accuracy, notwithstanding that the latter, when every precaution is taken, is perhaps theoretically more accurate.

Copper Assay by the Iodide Method.

Prepare a solution of sodium hyposulphite containing about 19 grms. of the pure crystals to the litre. Standardise as follows:—Weigh accurately about 0.200 gm. of pure copper foil, and place in a flask of about 250 c.c. capacity. Add 5 c.c. of a mixture of equal volumes of strong nitric acid (1.42 sp. gr.) and water, and thoroughly boil off the red fumes—a very essential point. Now remove from the lamp and add 6 to 7 grms. of crystallised zinc acetate, roughly weighed, and about 15 c.c. of water. Instead of adding the zinc acetate in this way, a cold saturated solution may be kept on hand and about 20 c.c. taken, the additional 15 c.c. of water being then unnecessary. Heat to boiling for a moment and then cool to ordinary temperature, and dilute to a bulk of about 50 c.c. Now add about 3 grms. of potassium iodide and shake it about gently until dissolved. Cuprous iodide will be precipitated, and iodine liberated according to the following reaction:—



The free iodine colours the mixture brown. Titrate at once with the hyposulphite solution until the brown tinge has become weak, and then add sufficient starch liquor to produce a marked blue colouration. Now continue the titration cautiously until the blue tinge has entirely vanished. When almost at the end allow a little time after the addition of each drop to avoid passing the point. One c.c. of the hyposulphite solution will be found to correspond to about 0.005 gm. of copper. In the assaying of ores, &c., when half a gm. is taken, 1 c.c. of the standard hyposulphite would then equal about 1 per cent copper. The reaction between the hyposulphite and the iodine is—



Sodium iodide and tetrathionate are formed. The starch liquor may be made by boiling about half a gm. of starch

with a little water, and diluting with hot water to about 250 c.c. It should be used cold, and must be prepared frequently for regular work, as it does not keep very well. The hyposulphite solution made of the pure crystals and distilled water appears to be very stable, showing no appreciable variation at the end of a month, when kept under reasonable conditions.

Treatment of Ores.

Treat half a gram. of the ore in a flask of 250 c.c. capacity with 5 or 6 c.c. of strong nitric acid, and boil gently nearly to dryness. Then add 5 c.c. of strong hydrochloric acid, and again boil. As soon as the incrustated matter has dissolved, add 5 c.c. of strong sulphuric acid and heat strongly, best by manipulating the flask in a holder over a small naked flame, until the more volatile acids are expelled and the fumes of the sulphuric acid are coming off freely. Allow to cool, and then add 20 c.c. of cold water, and heat the mixture to boiling, to thoroughly dissolve any anhydrous sulphates of iron, &c. Now filter to remove more especially any lead sulphate, and receive the filtrate in a beaker about 2½ inches in diameter. Wash the flask and filter with hot water, and endeavour to keep the volume of the filtrate down to about 50 or 60 c.c. Place in the beaker two pieces of sheet aluminum, which, for the sake of convenience in subsequent washing, may be prepared as follows:—Stout sheet aluminum, say about 1-16th of an inch in thickness, is cut into pieces an inch and a half square, and then the four corners are bent, for about a quarter of an inch, alternately up and down at right angles. This scheme prevents the pieces from lying flat against each other or upon the bottom of the beaker, and their washing is thus facilitated. The same pieces of aluminum may be used repeatedly, as they are but little attacked each time. Add 5 c.c. of strong sulphuric acid, cover the beaker, and heat to boiling. Boil strongly for about seven minutes. Unless the bulk of the solution is excessive, this will be quite sufficient with all percentages of copper. Ordinarily the aluminum will be found to be clean, and nearly or quite free from precipitated copper. If, by chance, the copper adheres to any considerable extent, it will usually become loosened by a little additional boiling, or it may be removed by the aid of a glass rod. Transfer the solution back to the original flask, and, by means of a wash-bottle of hot water, rinse in also as much of the copper as possible, leaving the aluminum behind. Drain the beaker as completely as possible, and temporarily set it aside with the aluminum, which may still retain a little copper. Allow the copper in the flask to settle, and then decant the liquid through a filter. Again wash the copper similarly two or three times with a little hot water, retaining it as completely as possible in the flask. Finally, wash the filter once or twice and endeavour to rinse all metallic particles down into the point. Now pour upon the aluminum in the beaker 5 c.c. of a mixture of equal volumes of strong nitric acid (1.42 sp. gr.) and water, and warm the beaker gently, but do not heat to boiling, as the aluminum would be thereby unnecessarily attacked. See that any copper present is dissolved, and pour the warm solution through the filter last used, thus dissolving any contained particles of copper, and receive the filtrate in the flask containing the main portion of the copper. At this stage do not wash either the aluminum or the filter, but simply remove the flask and set the beaker in its place. Heat the mixture in the flask to boiling, and see that all the copper is dissolved. Then add about half a gram. of potassium chlorate, and again boil for a moment. This is to oxidise any arsenic present to an arsenic acid, and is a very important point. Remove the flask from the lamp, and again place it under the funnel and wash the beaker, aluminum and filter with as little hot water as possible. Again boil sufficiently to remove every trace of red fumes. All the copper is now in the flask as nitrate. Add the zinc acetate, and proceed from this point precisely as described with the original nitrate

of copper solution in the standardisation of the hyposulphite, finally calculating the percentage of copper present from the amount of standard hyposulphite required. One point, however, remains to be further explained. According to the equation previously given, half a gram. of pure copper requires 2.62 grms. of potassium iodide. While direct experiment shows this to be apparently true, yet it is found that with small percentages of copper, the reaction, when only the theoretical amount of potassium iodide is taken, is slow, and in fact does not appear to proceed to completion until during the titration, which is thereby unduly prolonged. It is therefore best to use not less than 3 grms. of potassium iodide in any case. An excess does no harm. Silver does not interfere with the method. Lead and bismuth are without effect, except that by forming yellowish iodides they may mask the end-point before adding starch. Lead is practically removed as sulphate at a previous stage. If bismuth is suspected in any appreciable amount, simply add the starch earlier in the titration. Arsenic when oxidised as described has no influence. The return of the blue tinge in the liquid by long standing after titration is of no significance; but a quick return of the colour, which an additional drop or two of the hyposulphite does not permanently destroy, may indicate either an incomplete combination of all the nitric acid with zinc, or a failure to completely boil off the red fumes when dissolving the copper in nitric acid. The assay in such a case is spoiled. This trouble may be avoided by carefully following the directions given, and not guessing at strengths or quantities. The amount of zinc acetate recommended is a safe excess. Sodium acetate does not appear to work as satisfactorily.

For the assay of alloys, &c., the necessary modifications of the foregoing scheme are obvious.

The foregoing scheme directs the use of 5 c.c. of dilute nitric acid for dissolving the copper previous to titration, and prescribes 6 to 7 grms., or about 20 c.c., of a saturated solution of zinc acetate as a safe excess of neutralising agent. It is obvious that if most of the nitric acid be boiled away, the amount of zinc salt necessary is greatly reduced. In such a case, however, it is perhaps best, for safety's sake, not to use less than one-half the prescribed quantity. Half the zinc salt may thus be saved at the expense of a little more time. This is the ordinary practice in my own laboratory.—*Journal of the American Chemical Society*, vol. xviii., No. 5.

A HYPOTHESIS ON THE ATOMIC MOTION OF THE ELEMENTS AND ON THEIR ORIGIN.

By FLAVIAN FLAVIZKY.

THIS paper requires the five accompanying figures. The main proposition of the hypothesis is:—"The atoms of each element describe closed curves, which lie in planes respectively parallel and having a constant absolute position in space. The atoms of different elements move in planes which form with each other definite constant angles.

My hypothesis explains, not only the essential phases of chemical affinity, especially elective affinity and valence, but the periodic law itself is deduced as the consequence of a periodic change of the positions of the planes of atomic movements occurring with the increase of atomic weight.

This hypothesis is very closely connected with the question of the formation of the elements. If we assume the existence of a primitive matter, we must regard the elements as originating by an aggregation of the primitive matter. In this formation of the elements the primitive matter lost in part its motive energy. The atoms of the primitive matter, which in the beginning moved in the

most various directions, received a more regular motion in definite plane tracks. Such an orientation of movement could not take place under the influence of gravitation; we must suspect the action of a selective dualistic force, such as we meet in the phenomena of electricity.

In fine, I must make some remarks on the new elements which do not adapt themselves to the periodic system. Between the elements which follow the periodic law we always find elements with opposite properties, since most inactive nitrogen combines directly with boron, titanium, &c.; the recently discovered elements helium and argon appear more inactive than nitrogen. The peculiarities of the new elements depend perhaps on the character of their atomic movements not possessed by the ordinary components of the movements of other elements.

Hence we must conclude that helium and argon must have originated under different conditions, since their atomic motion takes place, not in closed curves, but perpendicularly to a plane the position of which may be regarded as intermediate among the positions of the planes of motion of the most energetic elements, such as the alkaline metals and the halogens. In this peculiarity of atomic motion we have perhaps the reason why the law of the entire rational relations of the atoms does not hold good for the new elements.—*Zeitschrift für Anorg. Chem.*, xii., Part 3, p. 182.

A STUDY OF THE ZIRCONATES.*

By F. P. VENABLE and THOMAS CLARKE.

(Concluded from p. 44).

IV. Fusion of Zirconia with Chlorides.

THIS method was used by Hiortdahl in preparing the zirconates of magnesium and calcium, and by Ouvrard for the same, and also for strontium, barium, and lithium. According to the latter they all gave zirconates of the form M_2ZrO_3 .

1. *Fusion with Sodium Chloride.*—There appeared to be very little action. The fusion was washed with water until free from chlorine. It was then treated as in the case of the carbonates. When 2 grms. of zirconia were fused with 16 grms. of sodium chloride, it was found that less than 2 per cent had been dissolved. In a second experiment, after heating six hours, the amount dissolved was less than 2-10ths of a per cent.

2. *Fusion with Potassium Chloride.*—No action was observable. When 2 grms. of zirconia were heated a number of hours with an excess of potassium chloride, and the mass then treated as above, only 3-10ths of a gm. had been acted upon. There seemed to be even less action in the case of lithium chloride at the temperature attainable by means of an ordinary water-blast lamp.

3. *Fusion with Alkaline Earths.*—Two attempts were made to prepare magnesium zirconate by fusing zirconia with magnesium chloride and ammonium chloride. It was not possible to prevent decomposition of the magnesium chloride. There seemed to be some action, but much difficulty was experienced in separating the products. The method described by Ouvrard gave evidences of zirconium in the washings.

In the case of fusions with calcium chloride no action could be observed. Two experiments were made, following closely the directions of Ouvrard, except as to temperature possibly, as to which no exact directions were given. A water-blast lamp was used for several hours. After leaching and washing, the mass left behind gave no zirconium to hydrochloric acid.

Our experiments with the chlorides have led us to believe that there is little or no action between zirconia and the chlorides of the alkalies or alkaline earths, except

where these chlorides are decomposed by the heat and oxides formed. Any action noticed is to be attributed to the oxides.

V. Precipitation from the Solution of a Zirconium Salt by means of an Alkaline Hydroxide.

Watts speaks of this method, but no experiments are recorded. It seemed to us, upon examination of the question, that very little evidence as to the existence of the zirconates or their properties could be drawn from such a method of preparation as this. It has been repeatedly observed that the precipitate formed by means of ammonium hydroxide is extremely hard to wash free from ammonia. After a very large number of washings, however, it is practically free from ammonia. The same is true of sodium and potassium hydroxides. Is it to be inferred that a definite zirconate is precipitated? At what point shall the washing be stopped, for manifestly some washing is necessary? Equally it cannot be decided because of this loss of alkali by prolonged washing, that we have a decomposition of the zirconate caused by the action of the water. It therefore seemed to be quite useless to make analyses of the precipitates gotten with different degrees of washing, — especially as somewhat similar experiments were carried out under the next heading.

VI. The Solution of Zirconium Hydroxide in Caustic Alkali.

It was found that zirconium hydroxide was perceptibly soluble in solutions of potassium and sodium hydroxide. Experiments were first made with a view of determining the extent of this solubility. Solutions of the two alkalies were made up of different strengths, an excess of zirconium hydroxide added, and the solution then boiled. After cooling, a measured quantity of the solution was drawn off, and the amount of zirconia present determined.

A 50 p. c. solution potassium hydroxide dissolved				
				Grm. per c.c.
33	"	"	"	0.00233
25	"	"	"	0.00097
25	"	"	"	0.00075
12	"	"	"	0.00009

In the case of sodium hydroxide there seemed to be a stronger solvent action:—

A 33 per cent solution dissolves				
				Grm. per c.c.
25	"	"	"	0.00245
25	"	"	"	0.0012
12	"	"	"	0.0005

If a concentrated solution of alkali, saturated with zirconium hydroxide, is diluted, a portion of the zirconium will be precipitated. Neutralisation with acid will also cause a precipitation of the zirconium. In both cases alkali is retained by the precipitate in spite of washing. Analyses were made of some of these precipitates after very thorough washing (in no case was less than a litre of water used). The results in four experiments were sufficient to show that these precipitates were practically zirconium hydroxide with a varying percentage of alkali, this percentage ranging from 1.15 to 3.94. It is possible to assume that zirconates were formed, and then decomposed by the action of the water during the washing; but it seems more probable that this is, as is true in the case of so many hydroxides precipitated by alkaline hydroxides, merely a stubborn retention of alkali. Assuming that the strong alkaline solutions held zirconates in solution, attempts were next made to prepare other zirconates by precipitation from them.

The addition of solutions of various salts gave small precipitates which seemed to be formed mainly because of the dilution of the alkaline hydroxide, and to consist almost entirely of zirconium hydroxide. It was necessary, therefore, to use strongly alkaline solutions of the compounds of the elements to be experimented with,

This greatly diminished the choice of compounds. Concentrated solutions of aluminum and zinc hydroxides in potassium hydroxide gave precipitates, but they were in too small amounts for reliable analyses to be made.

Summing up the results of the experiments performed, it is clear that the method yielding the best results for the preparation of the zirconates is fusion of gently dried zirconia with hydroxides or prolonged heating with the oxides. In the case of the alkaline earths this yields zirconates containing one equivalent of each oxide, as CaO.ZrO_2 , &c. The same is true of the magnesium compound. For lithium the compound obtained was LiO.ZrO_2 . For the alkalis it seemed to be possible to obtain only zirconates having a largely preponderating proportion of zirconia. There seems to be a tendency toward the formation of distinct compounds under certain conditions. These polyzirconates, and the lithium compound also, may be decomposition products due to the action of the water used in leaching. No other mode of separation from the products of the fusion could be devised by us, however. If they are produced by the decomposing and solvent action of the water, it is a little strange that a point should be reached beyond which the leaching extracted no more alkali, and that this point varied with changed conditions. This is not the case where zirconium hydroxide has been precipitated by an alkali.

Double Zirconates.

Two attempts at the formation of double zirconates were made.

1. *Potassium Calcium Zirconate.*—About 2 grms. each of zirconia, potassium hydroxide, and lime were heated together for about four hours. There was evidence of considerable action. The mass was treated with dilute acetic acid and thoroughly washed. Then, on treatment with dilute hydrochloric acid, nearly the whole residue went into solution. The analysis gave ZrO_2 , 67.21 per cent; CaO , 31.06; K_2O , 1.11. This is a calcium zirconate (CaO.ZrO_2), with a small part of the CaO substituted by K_2O .

2. *Potassium Aluminum Zirconate.*—Two grms. of zirconia were fused for eight hours with 2 grms. of potassium hydroxide and 3 grms. of alumina. The mass was washed with dilute acetic acid until no more alumina was dissolved. The residue was treated with dilute hydrochloric acid, and the insoluble portion removed by filtration. The analysis gave ZrO_2 , 72.38 per cent; Al_2O_3 , 7.66; K_2O , 20.00. These experiments indicate the possible existence of double zirconates, and when time admits this point will be further examined.

THE ACTION OF LIGHT ON SOME ORGANIC ACIDS IN THE PRESENCE OF URANIUM SALTS.*

By HENRY FAY.

Historical.

THE early history of photo-chemical reactions is involved with the history of photography. Schulze, in 1727, proved experimentally that the darkening of silver salts is due to the action of light; and, in 1799, Scheele ("Traité de l'Air et de Feu") showed the effects of different parts of the spectrum. It had been noticed several centuries before that silver salts are subject to change, but the work of Schulze was the first conclusive evidence that this change is due to the action of light. In the early part of this century the action of light on plant growth was

studied by many investigators who received the incentive from a suggestion made by Priestley.

Certain physical phenomena were early noticed, as the effect on crystallisation by Petit (*Mém. de Paris*, 1722), who showed, in 1722, that solutions of potassium nitrate and ammonium chloride crystallise more readily in the sunlight than in the dark. These effects were studied more carefully by Chaptal (*Journ. de Phys.*, vol. xxiv.) and Dize ("Sur la Crystallisation, &c.," 1789). In 1848, Becquerel (*Ann. Chim. Phys.*, [3], ix., 257) published his excellent researches on the phosphorescence of the sulphides of barium, calcium, and strontium, but none of these researches threw any light on the chemistry of the reactions caused by sunlight. Photography was being developed in the early part of the century and various effects were noticed, but the chemistry involved was not worked out. During this period many inorganic salts were found to undergo some change when exposed to the sunlight, and in general this change was a reduction, especially if there was an oxidisable organic substance present.

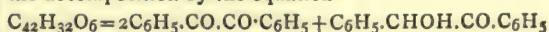
Among the salts most extensively studied were those of uranium. Before taking up the study of the reactions involved when uranium salts are decomposed in the sunlight, it will be well to review the work which has been done on the organic substances which are subject to change when exposed to the light. Many observations have been recorded in which the fact is simply stated that certain substances are sensitive to light, but only in a few cases has the reaction been a clear one. In the cases studied the reactions can be classified under one of these three heads—substitution, direct combination, and polymerisation.

Dumas (*Ann. Chim. Phys.*, [2], lxxiii., 77) has shown that the hydrogen atoms of the methyl group in acetic acid can be replaced by chlorine when the two substances are brought together in the direct sunlight, forming a substituted acetic acid. Phenomena of a similar nature were brought out by Schramm (*Ber. d. Chem. Ges.*, xviii., 350, 606, 1272; xix., 212), who has shown that when aromatic hydrocarbons having a side chain are treated with chlorine in the direct sunlight the substitution always takes place in the side chain.

Under the second head come the researches of Cahours (*Compt. Rend.*, xxiii., 1070), who prepared perchlormethyl oxalate and formate by bringing together the acids and alcohol in presence of chlorine. When exposed to the sunlight, the reaction takes place, forming the ethereal salts.

Chastaing (*Ann. Chim. Phys.*, [5], xi., 145) exposed acetic and butyric acids with alcohol, and by means of titration was able to measure the rate of etherification.

Somewhat similar are the facts discovered by Klinger (*Ann. Chem. (Liebig)*, ccklix., 137), who showed that aldehyds have the power of combining with phenanthrenequinone. He also noticed that if a reducible substance is exposed to light in presence of an oxidisable one, the solvent is oxidised while the substance in solution is reduced. By this means Klinger was able to convert phenanthrenequinone into phenanthrenehydroquinone, and at the same time the solvent, ether, was oxidised to acetic aldehyd. He found that benzil in ether solution passed over into a substance which he called benzilbenzoin, on account of the ease with which it can be broken down into these two substances. He represents the decomposition by the equation—



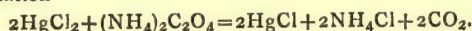
Under the head of polymerisation come the facts discovered by Lemoine (*Compt. Rend.*, xciii., 514). He found that chloral and styrolene are polymerised when exposed to the sunlight. Similar facts have been noticed in the field of inorganic chemistry, as in the case of phosphorus and sulphur. Yellow phosphorus is converted into the red modification, and a solution of sulphur in carbon bisulphide deposits the insoluble modification.

* From the author's Thesis, submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy, June, 1895. The work was undertaken at the suggestion of Professor Remsen and carried on under his supervision. From the *American Chemical Journal*, xviii., No. 4.

The work of Tyndall (*Proc. Roy. Soc.*, xvii., 92, 104) on light reactions cannot be placed under any of these heads, as the nature of the reaction is not known. He exposed the vapour of amyl nitrite to a beam of light and found that there was decomposition; oxides of nitrogen were formed, but the other products were not examined. Tyndall also found that allyl iodide and isopropyl iodide are affected by light, but he did not study the subject from its chemical side.

Oxalic acid has been extensively used in photo-chemical reactions, especially in form of its salts, and it has been recommended as a means of determining the amount of sunlight. Döbereiner (*Schweigger's Journ.*, lxii., 90) proposed to use ferric oxalate as a photometer in which the ferrous oxalate or the carbon dioxide given off could be measured. He also found that oxalic acid will reduce platinum chloride to metal, and that silver oxalate is partially reduced to metal.

Eder (*Wein. Academy Ber.*, ii., 1879) used as a photometer a solution of ammonium oxalate and mercuric chloride, which, on exposure to sunlight, gives off carbon dioxide and deposits mercurous chloride according to the equation—



Having reviewed briefly the effects of light on certain organic substances, the history of the reactions which involve the use of uranium salts will be given in detail. The first person to find that uranium salts are sensitive to light was Bucholz (*Ann. Chim. Phys.*, [I], lvi., 142), who described (1805) certain effects produced by the sulphate and alcohol. He says:—"Uranium sulphate dissolves in 25 parts of alcohol, and the solution undergoes remarkable changes on exposure to the sunlight; the yellow liquid becomes turbid and deposits a greyish green substance. After several days exposure the solution acquires an odour of nitric ether; the filtrate is colourless and contains no uranium; the precipitate of a green colour and retains sulphuric acid." Bucholz further observes that an ether solution of uranyl nitrate becomes green on exposure to sunlight, and a black substance is deposited.

Chemists added little to these results until Ebelman (*Ann. Chem. (Liebig)*, xliii., 294), in 1831, took up the subject. He confirmed the results of Bucholz with the uranium sulphate and alcohol, but noticed in addition that green crystals were formed, which he said were uranium protoxide. The precipitate he called the bibasic sulphate of the protoxide, and gave it the formula $2\text{UO}_3 \cdot \text{SO}_3 + 2\text{H}_2\text{O}$.

Uranium oxalate was also investigated by Ebelman. He observed that a solution of uranyl oxalate decomposed into a brown substance, which he believed to be the hydrated oxide, and into carbon dioxide and carbon monoxide in changing proportions.

St. Victor and Corvissart (*Compt. Rend.*, xxi.; *Ann. Chem. (Liebig)*, xliii., 114), working on the action of light on organic substances, noticed that if a solution of oxalic acid is exposed to the light it will quickly reduce a gold solution. They heated to boiling a 4 per cent solution of oxalic acid with a 1 per cent solution of uranyl nitrate, finding that in the dark no decomposition would take place, but after exposing to the sunlight action soon began. They say that carbon monoxide was given off, but do not mention having obtained any carbon dioxide. Another fact of interest discovered by them was that a small quantity of uranyl nitrate increased ten-fold the action of light on any amylaceous matter, converting it into dextrin and glucose.

Seekamp (*Ann. Chem. (Liebig)*, cxiii., 113) repeated the work of St. Victor and Corvissart, and found that after a solution of uranyl nitrate and oxalic acid had been exposed to the light for some time there was a deposit of a green crystalline powder; the solution became colourless and showed an acid reaction. The acid was identified as formic acid by means of its lead and barium salts.

From succinic acid he obtained carbon dioxide and propionic acid, and the precipitate which was formed he believed to be uranous succinate. Butyric acid and carbon dioxide were obtained from pyrotartaric acid.

H. C. Bolton (*Am. Journ. Sci.*, [2], xlviii., 206) in a review of the work done on uranium salts in photo-chemical reactions, adds some interesting facts discovered while working with certain uranium salts in photographic processes. He obtained a salt which is the double oxyfluoride of uranium and potassium, having the composition represented by the formula $2\text{UO}_2\text{F} + 3\text{KF}$. A solution of this salt acidified with formic acid decomposes in the sunlight, forming a precipitate which gives the formula $4\text{UF} + \text{KF}$. Oxalic acid causes a similar reduction, but with the formation of Ebelman's violet hydrate. Solutions of the nitrate, sulphate, oxychloride, and oxyfluoride are reduced when mixed with glycerin and placed in the sunlight. Even in the dry state, the uranium-ammonium citrate was found to be sensitive to light.

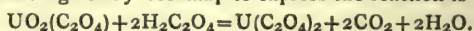
Wisbar (*Ann. Chem. (Liebig)*, ccxxxii., 262) next took up the study of light on uranium salts. He verified Seekamp's work on pyrotartaric acid, and showed, in addition, that butyric acid in presence of uranium salts breaks down into propane and carbon dioxide.

Somewhat similar to the work of Wisbar is that of Louis Lucien Bonaparte (*J. Prakt. Chem.*, xxx., 308), who obtained a decomposition of valeric acid by exposing it with a solution of uranyl valerate. The products formed he believed to be uranous valerate, and gases which he believed to be carbon dioxide, carbon monoxide, and a hydrocarbon.

Chastaing (*Ann. Chim. Phys.*, [5], xi., 145) studied the effect of the red and violet rays of the spectrum on solutions of uranyl nitrate and alcohol, and noticed the odour of aldehyd, which is probably the odour Bucholz took for nitric ether. Some uranyl acetate was formed in the solution.

At the suggestion of Prof. Remsen, H. C. Jones, working in this laboratory, undertook some time ago the study of the action of light on oxalic acid in the presence of uranium salts. As the results of his work have not been published, a short account of the results which he obtained will be given.

He verified the statement of Seekamp that, in the presence of uranium oxalate, oxalic acid is broken down into carbon dioxide, carbon monoxide, and formic acid. The equation given by Seekamp to express the reaction is—



Seekamp (*Ann. Chem. (Liebig)*, cxiii., 115) thought that the green compound precipitated was uranous oxalate, of the composition $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$.

A series of experiments was made by Jones in which varying amounts of uranyl oxalate and oxalic acid were used. The amount of carbon dioxide found in every case agreed to within a few c.c. with the amount of carbon dioxide which would have been liberated from the oxalic acid used, had it decomposed directly into carbon dioxide, carbon monoxide, and water. The amount of carbon monoxide set free, plus the amount combined as formic acid, was always somewhat less than the carbon dioxide.

The composition of the precipitate formed was found to depend on the amount of uranyl oxalate relatively to the free oxalic acid originally used. In all cases where a very large excess of oxalic acid was not used, it could be clearly seen that the precipitate was a mixture of crystals and an amorphous mass.

Analyses of the precipitate formed from various mixtures confirmed the belief that the precipitate was a mixture. When a solution containing 3 grms. of uranyl oxalate and 30 grms. of oxalic acid had been exposed to the light for a time, it was noticed that green crystals were forming on the bottom and sides of the flask. The solution was then removed from the direct sunlight, and allowed to stand in diffused light for some time, when a

considerable quantity of the crystals was obtained free from impurities. An analysis of the crystals dried between filter-paper gave 45.05 per cent uranium, which agreed fairly well with the composition $U(C_2O_4)_2 \cdot 6H_2O$, which requires 45.8 per cent of uranium, on the basis $U=240$, $C=12$, $O=16$.

Finally, a solution was prepared containing 3 grms. uranyl oxalate and 45 grms. oxalic acid. Pure crystals were obtained, as described above, which contained 46.05 per cent of uranium. It thus appears that the crystalline compound is formed pure only when a very large excess of oxalic acid is used.

It was then hoped that, by using a large amount of uranyl oxalate relatively to oxalic acid, the amorphous compound might be obtained in pure condition. For this purpose a solution containing 2 grms. of uranyl oxalate and 2 grms. of oxalic acid were exposed to the light. A greenish mass was at first precipitated, which, on longer exposure, became purplish brown. A solution of uranyl oxalate exposed alone to the direct sunlight apparently underwent the same transformation.

It was found, further, that a very small amount of uranyl oxalate will decompose a very large, if not an unlimited, amount of free oxalic acid if exposed continuously to the direct sunlight. If not continuously, the crystalline compound will separate out of the solution and the action will cease. Thus the reaction suggested by Seekamp, and given above, cannot express the whole truth, since, according to it, one molecule of uranyl oxalate can decompose only two molecules of free oxalic acid.

The uranyl salt seems to act in some way as an oxidising agent, as is indicated by the fact that the product precipitated is some reduction-product of the uranyl compound originally used.

Decomposition of Oxalic Acid in the presence of Uranyl Oxalate.

As the nature of the precipitate formed when oxalic acid is exposed to the sunlight in presence of uranyl oxalate was not cleared up by Jones on account of lack of time, it was decided, at Prof. Remsen's suggestion, to continue the work and study the products of decomposition. For this purpose, solutions containing oxalic acid and uranyl oxalate in varying proportions were exposed to the direct sunlight, and in all cases it was found that after considerable gas had been given off the solution became cloudy, and then deposited a light green crystalline powder. When all the oxalic acid was decomposed, and the evolution of gas had ceased, the remainder of the uranium in solution was deposited as a flocky purplish brown substance. Evidently, concordant results could not be obtained by working with the precipitate as a whole, and it was decided to remove the light green coloured precipitate when first formed.

To obtain it, 3 grms. uranyl oxalate and 2 grms. oxalic acid were dissolved in a litre of water, and exposed to the direct sunlight. When some of the green precipitate first formed had settled to the bottom of the flask it was filtered off, washed with water, and then dried between filter-papers. The dry substance has a very pale green colour, and showed no tendency to oxidation or change of any kind.

The uranium was determined by heating the substance in a porcelain crucible and weighing as the oxide U_3O_8 . In all of the analyses made this method was used; frequently, however, the oxide formed was converted into the nitrate, and the nitrate again decomposed. This was done simply to control the results, as the oxide U_3O_8 is more readily formed from the nitrate than from the uranium salt of organic acids.

The green-coloured substance gave these results:—

- I. 0.2637 grm. substance gave 0.1776 grm. U_3O_8 = 57.17 per cent U.
- II. 0.2015 grm. substance gave 0.1369 grm. U_3O_8 = 57.68 per cent U.

III. 0.2560 grm. substance gave 0.1725 grm. U_3O_8 = 57.20 per cent U.

Calculated for $U(C_2O_4)_2$, 57.69 per cent U.

This shows the substance to be uranous oxalate. It can be obtained at any time, provided the solutions be continuously exposed to the sunlight, and not too large an excess of oxalic acid be present. It was shown by Jones that when a large excess of oxalic acid is present, and the solution removed after a short exposure to the light, there is a strong tendency to the formation of the crystalline product $U(C_2O_4)_2 \cdot 6H_2O$. If the solutions are exposed until all of the oxalic acid is decomposed, some of the purplish brown substance is then formed.

Desiring to obtain the purplish brown precipitate in pure condition, several attempts were made to get it from solutions containing oxalic acid and uranyl oxalate by removing the uranous oxalate formed and subsequent exposure, but in all cases the precipitate contained a mixture of the two precipitates. When uranyl oxalate in solution is exposed to the sunlight, the same purplish brown precipitate is formed, and it was decided to use the uranyl oxalate alone for the purpose of obtaining it.

Decomposition of Uranyl Oxalate.

Four grms. of uranyl oxalate were dissolved in a litre of water, and the solution filtered to get rid of a small amount of undissolved substance. The solution was exposed to direct sunlight, and within five minutes after exposure the clear yellow solution had become cloudy. The cloudiness increased rapidly. In half an hour there was a deposit of the purplish brown substance on the bottom and side of the flask nearest the source of light. There was no evolution of gas.

Thinking that possibly the solution held the gas, several attempts were made to collect any gas formed by attaching large tubes filled with uranyl oxalate solutions to nitrometers containing mercury. Under much reduced pressure, and even by gentle heating, it was impossible to collect any gas. The precipitate formed in the above solutions was filtered off, washed with water, and left to dry in the air. The brown substance on drying changed to yellow, so that it was impossible to prepare it in this way for analysis. Even on drying rapidly between filter-papers there was some change noticed. If the brown substance is allowed to stand in the flask in which it is precipitated the same change takes place, although not so rapidly. The filtrate was always neutral to litmus, and contained nothing but traces of uranium salts, which were thrown out on evaporation to small volume. It was impossible in any case to get the uranium precipitated entirely, although the portion remaining in solution was extremely small in comparison with the whole amount of uranium present.

(To be continued).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on July 6th, Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—The Right Hon. Lord Windsor, Mr. Herbert Page, F.R.C.S., and Mr. Alfred Stuart.

City and Guilds of London Institute.—The Executive Committee of the City and Guilds of London Institute have appointed Mr. W. E. Dalby, since 1891 University Demonstrator of Mechanism and Applied Mechanics at Cambridge, to the Professorship of Mechanics and Applied Mathematics at the Institute's Technical College, Finsbury, rendered vacant by the resignation of Prof. Perry. Mr. Dalby served a seven years apprenticeship in the locomotive works of the Great Eastern Railway and gained a Whitworth Scholarship in 1883. In 1884 he entered the service of the London and North Western Railway, graduated B.Sc. London in 1890, and in 1894 received the full degree of M.A. *honoris causa* from the University of Cambridge.

ALUMINUM ALCOHOLATES.

By H. W. HILLYER.

In work preparatory to using the method of Wislicenus and Kaufmann (*Ber. d. Chem. Ges.*, xxviii., 1323) for reduction in neutral solutions by use of amalgamated aluminum, observations were made which have led to the work of which this is a preliminary notice.

According to these authors amalgamated aluminum does not act on absolute alcohol, but can be preserved for use covered by absolute alcohol. By following their directions we obtained an amalgam having properties like those described; but in order to avoid all contact with the air and the degeneration of the amalgam, caused by its coating over with hydroxide, instead of an aqueous solution of mercuric chloride, a solution of mercuric chloride in absolute alcohol was used. When this was brought in contact with chipped aluminum an evolution of gas soon commenced, and instead of ceasing, as might have been expected, when the little water in the alcohol had been decomposed, it increased in rapidity, and the alcohol became heated nearly or quite to the boiling-point.

The action gradually became more moderate, but continued so long that on cooling the whole gelatinised. The most probable reaction is—



Knowing from the work of Gladstone and Tribe that aluminum alcoholates, in contrast to all other known alcoholates, can be distilled under diminished pressure, an attempt was made to distil the product obtained. After the alcohol, a grey distillate of mercury came over under 20 m.m. pressure, and then white fumes and an oily liquid solidifying in the receiver. The distillate contains much aluminum, but is greatly contaminated with mercury.

In the attempt to avoid the presence of mercury, which made the purification difficult, other salts soluble in alcohol were tried, but with no special result until, on using fuming stannic chloride, a reaction took place similar to that with the mercuric chloride. In this case spongy tin separated, a gas was rapidly evolved, and the liquid became quite hot. In both cases an application of external heat starts a new evolution of gas. When no more gas was evolved the alcohol was distilled off and the residue in the retort subjected to distillation under diminished pressure. A distillate was obtained rich in aluminum and containing no tin. Determinations of the amount of aluminum seemed to indicate that the substance might be aluminum hydroxydiethylate, $\text{Al}(\text{OC}_2\text{H}_5)_2\text{OH}$, but work on the action of ethyl alcohol was temporarily interrupted at this point. Two experiments with methyl alcohol gave good evolution of gas, but no substance could be distilled under a diminished pressure. The retort after distilling off the alcohol contained apparently nothing but aluminum oxide or hydroxide. Work with normal propyl alcohol has resulted in showing definitely that aluminum tripropylate is formed under similar conditions. An account of this work will soon be published in detail.

Isopropyl and amyl alcohol also react on aluminum in the presence of aluminum chloride and the spongy tin formed by its action on stannic chloride in solution in these alcohols. The aluminum is dissolved to give a solution from which it is precipitated, probably as hydroxide, on addition of water or by mere action of the moisture of the air.

The writer desires to reserve for the present the privilege of investigating the action of aluminum on alcohols to which mercuric chloride and stannic chloride have been added, and to investigate the action of sulphur dioxide and of hydrogen sulphide on the alcoholates thus formed. —*American Chemical Journal*, vol. xviii., No. 7.

INTERNATIONAL CATALOGUE CONFERENCE.

THE following delegates attended :—

Austria.—Prof. Ernst Mach, Mitglied der Kaiserlichen Akademie der Wissenschaften, Vienna; Prof. Edmund Weiss, Mitglied der Kaiserlichen Akademie der Wissenschaften, Vienna.

Belgium.—M. H. La Fontaine, Membre de l'Institut International de Bibliographie, Brussels; M. Paul Otlet, Membre de l'Institut International de Bibliographie; M. de Wulf, Membre de l'Institut International de Bibliographie.

Denmark.—Prof. Christiansen, Universitet, Copenhagen.

France.—Prof. G. Darboux, Membre de l'Institut de France; Dr. J. Deniker, Bibliothécaire, Muséum d'Histoire Naturelle, Paris.

Germany.—Prof. Walther Dyck, Mitglied der K. Bay. Akad. der Wiss. zu München; Prof. Dziatzko, Direktor der Universitäts Bibliothek, Göttingen; Prof. van 't Hoff, Mitglied der K. P. Akademie der Wissenschaften zu Berlin; Prof. Möbius, Mitglied der K. P. Akademie der Wissenschaften zu Berlin; Prof. Schwalbe, Direktor, Berlin.

Greece.—M. Avierinos M. Averoff, Greek Consul at Edinburgh.

Hungary.—Dr. Theodore Duka, Membre Académie Hongroise des Sciences, Buda-Pesth; Prof. August Heller, Librarian, Ungarische Akademie, Buda-Pesth.

Italy.—General Annibale Ferrero, Italian Ambassador in London.

Japan.—Assistant Professor Hantaro Nagaoka, University, Tokio; Assistant Professor Gakutaro Osawa, Medical College, Tokio.

Mexico.—Señor Don Francisco del Paso y Troncoso.

Netherlands.—Prof. D. J. Korteweg, Universiteit, Amsterdam.

Norway.—Dr. Jørgen Brunchorst, Secretary, Bergen Museum.

Sweden.—Dr. E. W. Dahlgren, Librarian, Kongl. Svenska Vetenskaps Akademien, Stockholm.

Switzerland.—M. C. D. Bourcart, Swiss Minister in London; Prof. Dr. F. A. Forel, Président du Comité Central de la Société Helvétique des Sciences Naturelles.

United Kingdom.—Representing the Government: Right Hon. Sir John E. Gorst, Q.C., M.P., Vice-President of the Committee of Council on Education. Representing the Royal Society of London: Prof. Michael Foster, Sec. R.S.; Prof. H. E. Armstrong, F.R.S.; Mr. J. Norman Lockyer, C.B., F.R.S.; Dr. Ludwig Mond, F.R.S.; Prof. A. W. Rücker, F.R.S.

United States.—Dr. John S. Billings, U.S. Army; Prof. Simon Newcomb, For. Mem. R.S., U.S. Nautical Almanac Office.

Canada.—The Hon. Sir Donald A. Smith, G.C.M.G., High Commissioner for Canada.

Cape Colony.—Roland Trimen, Esq., F.R.S.; Dr. David Gill, F.R.S.

India.—Lieut.-General Richard Strachey, R.E., F.R.S.

Natal.—Walter Peace, Esq., C.M.G., the Agent-General for Natal.

New South Wales.—Prof. Liversidge, F.R.S.

New Zealand.—The Hon. W. P. Reeves, Agent-General for New Zealand.

Queensland.—Chas. S. Dicken, Esq., C.M.G., Acting Agent-General for Queensland.

OPENING MEETING, Tuesday, July 14th, 1896, 11 a.m., at the Rooms of the Royal Society, Burlington House.

1. Prof. Foster (Sec. R.S.) moved that Sir J. Gorst act as provisional President for the purpose of organising the Conference.

2. The resolution, having been unanimously accepted, Sir John Gorst welcomed the Delegates.

3. Prof. Armstrong gave a brief account of the work done by the Royal Society in arranging for the Conference, as well as of the work to be accomplished.

The following resolutions were then agreed to:—

4. That each delegate shall have a vote in deciding all questions brought before the Conference.

5. That English, French, and German be the official languages of the Conference, but that it shall be open for any delegate to address the Conference in any other language, provided that he supplies for the *procès verbal* of the Conference a written translation of his remarks into one or other of the official languages.

6. General Ferrero moved that Sir John E. Gorst be the President of the Conference. The motion having been unanimously accepted,

7. Sir John Gorst nominated as Vice-Presidents—General Ferrero, Prof. Darboux, Prof. Mach, Prof. Möbius, Prof. Newcomb.

It was further resolved:—

8. That Prof. Armstrong be the Secretary for the English language. That Prof. Forel be the Secretary for the French language. That Prof. Dyck be the Secretary for the German language.

9. That the Secretaries, with the help of shorthand reporters, be responsible for the *procès verbal* of the proceedings of the Conference in their respective languages.

10. That the Conference adjourn at 1 p.m., and re-assemble at 2.30 p.m., continuing the sitting not later than 5 p.m.

11. That on Wednesday the Conference meet at 10 a.m., adjourning as before from 1 p.m. until 2.30 p.m.

The resolutions prepared by the International Catalogue Committee of the Royal Society to serve as a basis for discussion were then taken into consideration, and the following resolutions were agreed to *nemine contradicente*.

12. That it is desirable to compile and publish by means of some international organisation a complete Catalogue of Scientific Literature, arranged according both to subject-matter and to authors' names.

13. That in preparing such a Catalogue regard shall, in the first instance, be had to the requirements of scientific investigators, to the end that these may, by means of the Catalogue, find out most easily what has been published concerning any particular subject of enquiry.

14. That the administration of such a Catalogue be entrusted to a representative body, hereinafter called the International Council, the members of which shall be chosen as hereinafter provided.

15. That the final editing and the publication of the Catalogue be entrusted to an organisation, hereinafter called the Central International Bureau, under the direction of the International Council.

16. That any country which shall declare its willingness to undertake the task shall be entrusted with the duty of collecting, provisionally classifying, and transmitting to the Central Bureau, in accordance with rules laid down by the International Council, all the entries belonging to the scientific literature of that country.

17. That in indexing according to subject-matter regard shall be had, not only to the title (of a paper or book), but also to the nature of the contents.

18. That the Catalogue shall comprise all published original contributions to the branches of science hereinafter mentioned, whether appearing in periodicals or in the publications of Societies, or as independent pamphlets, memoirs, or books.

SECOND MEETING, Wednesday, July 15th, 1896, 10 a.m., at the Rooms of the Royal Society, Burlington House.

19. It having been proposed—

That a contribution to science for the purposes of the Catalogue be considered to mean a contribution to any of the mathematical, physical, or natural sciences, the limits of the several sciences to be determined hereafter.—

The following amendment was moved, and, after discussion, adopted:—

That the terms of the resolution be referred to a Committee, consisting of Messrs. Armstrong, Billings, Darboux, Korteweg, Möbius, and Schwalbe, to report to the Conference at the opening meeting, on July 16th.

The following resolutions were then agreed to, *nemine contradicente*:—

20. That in each country the system of collecting and preparing material for the Catalogue shall be subject to the approval of the International Council.

21. That in judging whether a publication is to be considered as a contribution to science suitable for entry in the Catalogue, regard shall be had to its contents, irrespective of the channel through which it is published.

22. That the Central Bureau shall issue the Catalogue in the form of "slips" or "cards," the details of the cards to be hereafter determined, and the issue to take place as promptly as possible. Cards corresponding to any one or more branches of science, or to sections of such sciences, shall be supplied separately at the discretion and under the direction of the Central Bureau.

23. That the Central Bureau shall also issue the Catalogue in book form from time to time, the entries being classified according to the rules to be hereafter determined.

That the issue in the book form shall be in parts corresponding to the several branches of science, the several parts being supplied separately, at the discretion and under the direction of the Central Bureau.

24. General Ferrero having moved—

That the Central Bureau be located in London—

The resolution was seconded by M. Darboux, supported by Messrs. Möbius, Heller, Weiss, Simon Newcomb, Olet, Duka, Bourcart, Dahlgren, and Korteweg, and accepted by acclamation.

THIRD MEETING, Thursday, July 16th, 1896, at the Rooms of the Royal Society, Burlington House.

The appointment of Prof. Liversidge, F.R.S., as official delegate representing New South Wales, was notified.

25. The following resolutions were agreed to *nemine contradicente*:—

That a contribution to science for the purposes of the Catalogue be considered to mean a contribution to the mathematical, physical, or natural sciences, such as, for example, mathematics, astronomy, physics, chemistry, mineralogy, geology, botany, mathematical and physical geography, zoology, anatomy, physiology, general and experimental pathology, experimental psychology, and anthropology, to the exclusion of what are sometimes called the applied sciences—the limits of the several sciences to be determined hereafter.

26. That the Royal Society be requested to form a Committee to study all questions relating to the Catalogue referred to it by the Conference, or remaining undecided at the close of the present sittings of the Conference, and to report thereon to the Governments concerned.

27. Since it is probable that, if organisations be established in accordance with Resolution 16, the Guarantee Fund required for the Central Bureau can be provided by voluntary subscriptions in various countries, this Conference does not think it necessary at present to appeal to any of the Governments represented at the Conference for financial aid to the Central Bureau.

FOURTH MEETING, Friday, July 17th, 1896, at the Rooms of the Royal Society, Burlington House.

The following resolutions were agreed to *nemine contradicente*:—

28. The Conference being unable to accept any of the systems of classification recently proposed remits the study of classifications to the Committee of Organisation.

The Belgian delegates expressly desired that it be

placed on record that they abstained from voting on this resolution.

29. That English be the language of the two catalogues, authors' names and titles being given in the original languages except when these belong to a category to be determined by the International Council.

30. That it be left to the Committee (of the Royal Society) to suggest such details as will render the Catalogue of the greatest possible use to those unfamiliar with English.

31. That it is desirable that the Royal Society should be informed, at a date not later than January 1st, 1898, what steps (if any) are being taken, or are likely to be taken, in the countries whose Governments are represented at the Conference, towards establishing organisations for the purpose of securing the end had in view in Resolution 16.

32. That the Delegates, in reporting to their respective Governments the Proceedings of the Conference, should call immediate attention to Resolutions 16 and 31.

33. That January 1, 1900, be fixed as the date of the beginning of the Catalogue.

34. That the Royal Society be requested to undertake the editing, publication, and distribution of a verbatim report of the Proceedings of the Conference.

35. That the *procès verbal* of the Conference be signed by the President and Secretaries.

36. That this Conference requests the Royal Society to express to my Lord Mayor of London and to Dr. L. Mond their grateful, hearty appreciation of the hospitality shown by them to the Delegates.

37. On the motion of M. Darboux, a vote of thanks to Sir John Gorst, for presiding over the Conference and his conduct in the chair, was passed by acclamation.

38. On the motion of Prof. Weiss, a vote of thanks to the Royal Society, for their cordial reception of the Delegates, was unanimously carried.

(Signed) { JOHN E. GORST, President.
HENRY E. ARMSTRONG,
WALTHER DYCK,
F. A. FOREL, } Secretaries.

OBITUARY.

THE LATE PROFESSOR AUGUST KEKULÉ.

THE 13th of the current month witnessed the death of August Kekulé—whose full name is Friedrich August Kekulé von Stradonitz.

This illustrious *savant* was born at Darmstadt in 1829, and was at first destined to become an architect. The lectures of Liebig induced him to turn his attention to chemistry. At Paris he was a pupil of Dumas, Wurtz, and Gerhardt. In London he met with Williamson, and became familiar with the more philosophical phase of our science.

In 1856 he became a privat docent of chemistry at Heidelberg. Two years later he succeeded to the chemical chair at Ghent; and in 1865 he succeeded A. W. Hofmann as Professor of Chemistry and Director of the Chemical Institute of the University of Bonn, an office which he filled up to his death.

His principal work, "*Lehrbuch der Organischen Chemie*" (Erlangen, 1861—1869) has not been completed, but like its companion work, "*Chemie der Benzole derivate*" (Erlangen, 1867), has contributed most essentially to the development of theoretical chemistry.—*Chemiker Zeitung*.

The Reward of Physical Research.—A mighty advertiser does honour to Prof. Röntgen by announcing the new X-rays camera as "the great joke of the day."

NOTICES OF BOOKS.

Incandescence by Gas and Petroleum. Acetylene and its Applications. By F. DOMMER, Professor at the School of Industrial Physics and Chemistry of the City of Paris. Paris: Bernard Tignol.

THE author considers that the struggle between the electric light and its rivals is far from being decided. Pointing to the system of Siemens and Wenham, to the incandescence burners of Auer, and the complete consumption burners of Bandsept and Denayrouse, he has much to advance, as far at least as the price of the illuminant is concerned. As regards acetylene, everything must depend on the price at which its source, calcium carbide, can be put on the market. M. Dommer is sceptical as regards the alleged quotation of 150 francs per ton.

He remarks that the eye is most sensitive to the yellow and green rays; the luminous intensity in the yellow being 1000, that of the ultra-violet is only 6, and that of the ultra-red 0.

Lights rich in violet and ultra-violet rays, like those of magnesium and the arc, are hurtful to the sight. These rays, in sunlight, occasion sun-stroke, or erythema, and contribute to the destruction of the fibres of the crystalline lens. Hence the production of violet rays, in sources of artificial light, should therefore be avoided.

Lights very rich in yellow rays tend to destroy the erythropsine, which is re-formed in darkness.

If we wish to distinguish forms we must adopt a reddish lantern rather than one giving a yellow light.

The ideal source of light would emit neither thermic radiations nor dark rays.

It is here declared that the final optical yield of the energy expended in an electric lamp is only about 1 per cent.

It is an interesting fact that the light of the firefly (*Lampyrus*) consists almost exclusively of yellow and green rays.

The photometers of Rumford, Bunsen, and Foucault are described and figured in Chapter IX., as also the standards officially adopted in different countries. The carcel is still employed in France, as is the spermaceti candle in Britain. It is remarked, truly enough, that this standard is liable to vary to the extent of 30 per cent. The pentane standard is not criticised. Germany employs the paraffin standard candle, and the amyl-acetate lamp invented by Von Hefner-Altenneck.

The absolute unit, proposed by Violle, is the luminous intensity emitted in the normal direction by a square centimetre of platinum in the temperature of solidification. It is equal to 2.08 carcel. The international unit, or "decimal candle," is the 1-20th of Violle's unit, and, like all candles, is liable to fluctuate. On the faith of experiments made in Paris, the Auer burner would appear more economical than the electric light, though a gas incandescence system would be still less expensive.

The second part of the work is devoted to acetylene, C_2H_2 , a compound discovered by Ed. Davy in 1836, and produced synthetically by Berthelot. The preparation of calcium carbide, on such a scale that it can be applied to the production of acetylene, seems due to Moissan and his assistant, Bullier.

Acetylene is a colourless gas with an odour of garlic, but agreeably ethereal if prepared from pure material. If a small primer of mercury fulminate is made to explode in the midst of this gas, it is decomposed with a violent explosion and a large flame.

It produces in equal volumes sixteen times more light than Paris gas burning in a normal Bengel burner. The amount of heat given out is, however, relatively less.

Berthelot has established that acetylene is an endothermic substance. If diluted with atmospheric oxygen it forms very dangerous explosive mixtures. It is very

apt to strike back into the mains or into the gasometers. To avoid this danger, the acetylene is diluted with nitrogen. The maximum explosive power is obtained with a mixture of 12 parts of air to 1 part of acetylene.

Acetylene is not more poisonous than the ordinary carbides forming ethylene, &c., or than coal-gas.

Coal-gas may be enriched by adding small quantities of acetylene not exceeding 5 to 6 per cent. At the price of 50 centimes per cubic metre acetylene may enter into practical use at gas-works.

The work before us is valuable as calling the attention of industrialists to a product which has possibly a great future.

An Inquiry into the Alleged Liability of Wood Charcoal to Spontaneous Combustion. Cartvale Chemical Co., Limited, Paisley. Third Edition, Revised. Paisley and London: Alex. Gardner.

The question here discussed is one of serious moment. If charcoal is, under unknown or undefined circumstances, capable of spontaneous explosion, the manufacture, carriage, and storage of gunpowder, *i.e.*, the old black powder, is attended with a source of danger not sufficiently appreciated.

It is, of course, necessary to note the exact sense of the term used in this discussion. The Cartvale Co. conclude from their own experiments and observations, as well as from correspondence with experts, that:—"Freshly made charcoal, *i.e.*, charcoal which has not absorbed its moisture and oxygen, is liable to so-called spontaneous combustion or re-ignition. After having absorbed its moisture and oxygen, which it does in the course of a few days, it is never liable to so-called spontaneous combustion." With this conclusion our own observations allow us to agree.

The Cartvale Chemical Co. prudently and justly confine their conclusion to wood-charcoal, with which alone they are practically concerned.

Bone-black, or animal charcoal, is much more liable to heating, and may even in chemical manures and composts give rise to actual combustion. Thus "spent" animal charcoal, though perfectly cool, and by no means absolutely free from moisture, and though largely mixed with mineral matter, has been known to "heat." From the point of view of fire insurance companies, spontaneous combustion comprises not only combustion from causes inherent in the material, but combustion arising from contact with oils water, acids, &c.; bulls'-eye windows and sun's rays converting these into magnifying (better, "burning") glasses; cotton-wool, greasy rags, &c., in mills.

If we remember the extreme liability of ground dyewoods to heat, we shall see that the question is not absolutely exhausted. These points, however, lie outside the purview of the charcoal burner and gunpowder manufacturer.

Chilian Review of Hygiene. ("Revista Chilena de Higiene"). Published for the Institute of Hygiene of Santiago. Director, Dr. F. PUGA BORNE. Tome II., October, 1895., No. 5. Santiago de Chile: Cervantes.

In attention paid to public health, as well as in other matters not a few, Chile is strikingly in advance of the other South American republics.

The present number contains an investigation of Eberth's bacillus in a defecation by a typhoid patient.

Then follows an account of the epidemic of typhoid fever in the hills Alegre and Concepcion and the Water of Quebrada Verde—a report presented to the magistracy of Valparaiso by L. E. Mourgues, M.D. (Paris).

The author found the water of the reservoir of San Agustín in a deplorable state. Nitrates and nitrites were both determined, as also free and albumenoid ammonia. The water was much contaminated with organic matters

of animal and vegetable origin, and the quantity of chlorine corroborated this conclusion. The micro-organisms found were *B. coli communis* and *B. typhi abdominalis*. Dr. Mourgues recommends filtration.

Another paper treats of pepper and its falsifications in Chile, and is illustrated with cuts of the chief adulterants, such as white and black mustard, linseed, shells of olives, nuts, almonds, and hemp seed, the fruit of buckthorn (*Rhamnus cathartica*), &c.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 1, July 6, 1896.

The Perpetual Secretary announces that the Institute being in definitive possession of the funds of the bequest of Jean Jacques Berger, the various Academies will be able, setting out from 1897, to award the Jean Jacques Berger prize to the most meritorious work concerning the city of Paris. For a first period of five years the prize awarded by each of the five Academies will be of the value of 12,000 francs. After the year 1909 the value of the annual prize will be raised to 15,000 francs. In 1899 the prize will be awarded by the Academy of Sciences.

The Academy proceeded to nominate a correspondent for the Section of Astronomy, *vice* Hind, deceased. Mr. Christie obtained the votes of all the members present and was proclaimed elected.

Researches on Tungsten.—Henri Moissan.—Will be inserted in full.

Solubility of Carbon in Rhodium, Iridium, and Palladium.—Henri Moissan.—Rhodium, palladium, and iridium, like platinum, readily dissolve carbon at the temperature of the electric furnace, abandon it in the form of graphite prior to solidification, and do not form carbides. All these graphites are capable of sprouting.

Opening a "Pli Cacheté."—M. Loiseau demanded the opening of a "pli cacheté" which he had deposited on March 6th, 1888. It bears the title "Note on certain Properties of Raffinose serving as the Basis of a Method for the Determination of that substance, of Dextrine, and of Saccharine in Sugary Products."

Refraction and Diffraction of the X Rays.—M. Gouy.—It is established with certainty that if diffraction exists as it does for light the wave-length of the X rays is considerably smaller than 0.005μ , which represents $\frac{1}{100}$ th of the wave-length of the green. Nothing indicates that there exists any diffraction whatever.

Action of Zinc upon a Photographic Plate.—R. Colson.—I have observed that zinc exerts upon platino-bromide an energetic action. If we clean with sand-paper a portion of leaf-zinc which has been left to itself for some time, and bring it into contact with a gelatino-bromide plate for about 24 hours, development causes a deep grey tint to appear opposite the cleaned part and of a lighter grey opposite the parts still bright though not recently cleansed, whilst scarcely anything appears opposite the oxidised parts. This action appears also at a distance and through certain bodies. The cause seems to be vapour of zinc. Magnesium and cadmium give the same effect, but nothing is obtained with lead, tin, copper, iron, and aluminium.

Action of Nitrogen Peroxide upon Antimony Tetrachloride.—V. Thomas.—Nitrogen peroxide does not combine with antimonious chloride. Antimony bromide, near its melting-point, gives rise to an escape of bromine if submitted to the action of nitrogen peroxide whilst the gas is absorbed.

Action of High Temperatures on certain Sulphides.—A. Mourlot.—By means of the electric furnace we have obtained the crystallisation of the lead, antimony, zinc, and cadmium sulphides. The two first mentioned are decomposed into pure metal without the formation of sub-sulphides.

On Two Isomers of Anethol.—Charles Moureu.—Ortho-anethol and meta-anethol, which form the subject of this paper, have not yet occurred in nature. Paranethol exists in abundance, and forms at least 19-20ths of the essence of aniseed met with in commerce.

Action of Ethyloxalyl on Naphthalene in presence of Aluminium Chloride.—L. Rousset.—The method with aluminium chloride has been, at the suggestion of M. Bouveault, applied to the naphthalene series with success. The author describes the products obtained.

Zeitschrift für Analytische Chemie.
Vol. xxxv., Part 1.

Reactions of the Pigment of Bacillus prodigiosus.—Bordoni Uffreduzzi.—The colour reactions of this bacillus agree partially with those of magenta. But the bacillus colour is brightened by mineral acids, is not changed by alkalis, and can be fixed upon wool in an alkaline solution.

Analysis of Yeast.—P. Guishard (*Bull. de la Soc. Chim.*).

Vegetable and Animal Oils in Mineral Oils.—W. de la Royère (*Revue des Falsifications*).—The author employs the property of very dilute solutions of rosaniline to form colouring matters with acids.

Determination of Sulphur in Pyrites.—(See CHEMICAL NEWS: T. S. Gladding, lxx., p. 181; G. Lunge, lxxi., p. 132; Frank Johnson, lxx., p. 212).

Determination of Sulphur in Roasted Copper Ores and Cupriferos Pyrites.—Keller and Maas (*Journal of the Franklin Institute*).

Valuation of Wool-Fat.—F. v. Cochenhausen (*Dingl. Pol. Journ.*).

Approximate Valuation of Crude Cresol.—A. Schneider (*Pharm. Central Halle*).

Volumetric Determination of Formaldehyd.—M. Klar (*Pharm. Zeit.*) has improved the operation by using as indicator congo-red.

Alkaloidal Reactions of Acetanilide.—E. Schär (*Archiv der Pharm.*).

Atomic Weight of Molybdenum.—Karl Seubert and W. Pollard (*Zeit. Anorg. Chemie*).—The mean value for molybdenum is 95.772, or, if reduced to a vacuum, 95.735.

Re-determination of the Atomic Weight of Yttrium.—Harry Jones.—If O=16 and S=32 the author deduces from his determinations the mean value for yttrium as 88.95.

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1915.

AN AUTO-PNEUMATIC STIRRER.

By H. BREARLEY.

In the laboratory of large steel works, carbon by combustion is an every-day requirement; it is, indeed, no uncommon thing to find one or two assistants engaged solely on this work, making from five to ten estimations per day. The most tedious part of the determination is the decomposition of the steel and the subsequent solution of the deposited copper. This is particularly true of low carbon steels and bar irons which bore lumpy.

The common practice, after adding the copper ammon. (potass. or sodic) chloride, is to use a glass rod for bringing fresh portions of the solution into contact with the metal, or, in better appointed laboratories, to use a mechanical stirrer, such as Taylor's "duplex circular" or the one described by Blair ("Chem. Anal. Iron," p. 139, 2nd edit.). Exposed to the fumes the metal parts of these become foul; they are rather expensive, take up considerable room, and sometimes throw out the solution.

The illustration itself almost explains the new form of stirrer. The centre bottle is exhausted through the elongated funnel by attaching to a Bunsen filter-pump, or simply an ordinary filter-tube. The borings and acidified copper solution (as recommended by Langley, CHEMICAL NEWS, lxi., 4) having been placed in the flask, the first one is attached to the "exhaust" bottle, the second one to the first, third to second, and so on according to the power of the pump.* The last one is attached to a wash bottle containing lead acetate solution, so as to free the air from carbonaceous grit and sulphuretted hydrogen. When the filter-pump is started the centre bottle is exhausted, and there is a continual passage of air through the whole series, to fill up the partial vacuum. This keeps the solution in constant motion, always bringing fresh portions into contact with the metal.

Two or more series may be run by fitting an additional tube into the exhaust bottle and regulating the pressure by clips, and the solution may be effected in beakers by fitting a bell-jar with smeared edges on to a ground-glass plate, placing the beaker thereunder, and passing the tubes through the stopper. But for most purposes flasks are preferable. I know of none so satisfactory for this and many other purposes as the "Registered Pattern Flask." The sole maker is Mr. J. Preston, Fargate, Sheffield. I am not aware that it has ever been previously described. It was designed by the present Principal of the New South Wales Metallurgical Department—James Taylor, B.Sc.—about thirteen years ago. It combines the advantages of the conical and globular flask,—that is, every part can be readily reached by a "policeman," and a small quantity of liquid for boiling covers the bottom. In this case it is especially useful, because, having a small base, the borings lie near the in-rushing bubbles and are the more thoroughly mixed with the solution.

It is important to note that there is no grinding of the carbonaceous residue. It largely retains the shape of the boring, and is so easily washed from the flask with a jet of water that a sample may be filtered and washed free from chlorides in fifteen minutes. We use a smooth funnel, with a $\frac{3}{4}$ -inch perforated platinum plate in the throat and covered with asbestos.

* We have a simple tube and 12 feet fall of water. A series of twenty is very readily agitated.

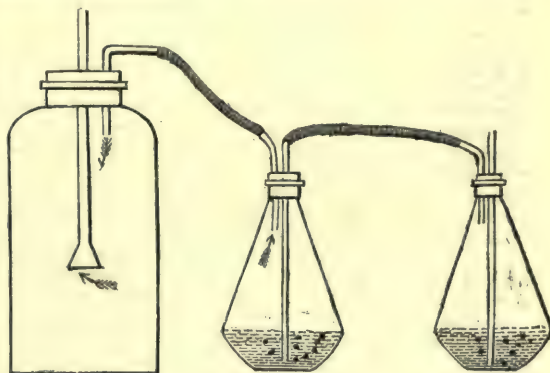
† Copper discs may be used, but they do not last long.

As generally dissolved, the carbonaceous residue in chromium and tungsten and much-worked steels has a very irritating tendency to run through the filter. Since March, 1895, amongst a great number of such steels there has been no trouble whatever, except in a solitary case, where we had to make a more compact filter than usual and wash with alcohol. With ordinary steels the residue is very coarse, and an open filter may safely be used. When the only sample of steel available has been too small to be bored—small screws, and the like—the residue has been perfect in form, even to the threads.

Eight or ten years ago we used a similar arrangement for recovering copper from residues. For two years it has been used for the purpose named, and personal experience—reaching to nearly a thousand estimations—has proved it to be satisfactory.

To sum up its advantages:—It is cheap, requires no power every laboratory is not equipped with, takes up no additional room, has no parts to be acted on by fumes, breaks no glass ware, facilitates subsequent operations, and effects the solution cleanly, effectively, and quickly.

We find it convenient to start the samples just before leaving the laboratory. A very gentle air-current dissolves them before morning.



Occasionally a carbon estimation by combustion is required very quickly in a sample of steel to which the colour method cannot be applied. In such cases the following procedure has been found very convenient:—Place sample and solution into flask as usual, and close the mouth with a solid stopper. Whirl the solution round and round by moving the flask in a small circle, now one way and now the other. In a few minutes, depending on the kind of borings and the percentage of carbon, the precipitated copper will have all dissolved, except a particle here and there. Wash the stopper, allow to settle five minutes or so, and filter, &c.

The annexed examples will give some idea of the rapidity with which samples may be prepared for combustion. Five grms. of steel were taken and between 350 and 400 c.c. of copper ammon. chloride—saturated solution.

Per cent C.	Time to dissolve.	To filter, wash Cl free, and boat.	Total.
I. 0.36	15 minutes.	15 minutes.	30 minutes.
II. 0.74	5 "	15 "	30 "
III.* 0.72	4 "	7 "	16 "

* Tungsten was present.

I. and II. were filtered immediately. About half-way through the filter choked somewhat, and the solution ran through in drops rather than a continuous stream. It is an advantage, from a speed point of view, to let the carbonaceous residue settle a few minutes (e.g., III. settled five minutes). An estimation may be made in from 1 to 1½ hours if the moist combustion process is used.

The Laboratory, Norfolk Works, Sheffield.

NOTE ON THE
COMMERCIAL PREPARATION OF BORON,
WITH REMARKS UPON
THE ELECTRO-CATALYTIC ACTION OF THE
ELEMENT.

By H. N. WARREN, Principal Boron Carbon Battery Co.

THE element boron, which up to the present date has ranked mainly as a chemical curio, chiefly on account of its costliness, has now shared a fate similar to so many of the hitherto scarcer elementary bodies which advanced science has thought fit to enrol under the title of ordinary.

An improved method for the preparation of this substance, which is now made in large quantity by the above Company (and which is entirely consumed in the preparation of boronised graphite used in the construction of their primary batteries) is brought about as follows:—

Boracic acid, after calcination, in order to deprive it of its water of crystallisation, and thus convert it into boron trioxide, is ground to a fine powder, and intimately mixed with a suitable proportion of magnesium sodium chloride; the mixture is now rapidly heated to fusion, and metallic sodium introduced from time to time in large pieces, and the mass well stirred after the introduction of each piece. The reaction thus afforded is extremely moderate, but intense heat is evolved; metallic magnesium in the first instance being set free, in accordance with the following equation:— $\text{MgCl}_2 + 2\text{Na} = 2\text{NaCl} + \text{Mg}$, which at once attacks the boron trioxide, forming MgO , and free boron, $3\text{Mg} + \text{B}_2\text{O}_3 = 3\text{MgO} + 2\text{B}$. The pasty mass thus formed is detached from the crucible and thrown into an excess of HCl , when all dissolves out save the boron, which is filtered, washed, and dried. After further heating in special atmospheres, the boron is procured peculiarly active; when impregnated with graphite resembling, to a certain extent, the surface action of platinum-black.

Carbons thus prepared, about 5 inches by 2, when arranged as an outer or positive element of a battery, and charged with chromic acid solution, have been found sufficiently effective to evolve over 5 ampères from each carbon. Small cells thus arranged, equal in size to a quart Bunsen cell, give over 240 amp.-hrs., or 25 ampères for twelve hours constant.

The general and most favourable depolarisers employed with these carbons is either a saturated solution of ferric chloride and oxide of manganese, which at the same time furnishes a recuperative solution, or, secondly, chromic acid, or the still more energetic action afforded by potassium permanganate when duly acidulated.

So great has been the demand for these primaries as a motive power, where great potential is required, together with quantity, that nearly a quarter of a million of carbons so prepared have been manufactured by the Company during this season, consuming several pounds of boron per week.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

ON THE
OCCURRENCE OF AMMONIACAL NITROGEN
IN PRIMITIVE ROCKS.

By HUGO ERDMANN,

DURING researches on argon and helium with which I have been engaged for some time, in concert with Prof. Dr. E. Dorn, the Director of the Physical Institute of Halle, it occurred to us that a series of minerals from Finland and Scandinavia displayed very distinctly, along with more or less helium, the bands of nitrogen when we

heated the pulverised mineral in a vacuum in admixture with potassium dichromate, and examined in a Plücker tube the gas evolved. As quite especial attention had been given to the absolutely tight fitting of our apparatus, the quantities of nitrogen observed could not be derived from the atmosphere.

This phenomenon was especially striking in two newly-discovered minerals from Finland, the one closely allied to polykrase and the other very similar to euxenite.

Whilst the latter mineral on spectroscopic examination displayed, along with the yellow and green helium lines, the lines of nitrogen only with moderate brightness, the Finnish polykrase, which contains no helium, evolved so bright and clear a spectrum of nitrogen that this mineral evidently contains nitrogen in a ponderable amount, and, as experiments showed, in the state of ammonia.

On a further examination it appeared that the occurrence of ammoniacal nitrogen in the northern primitive rocks is a very general phenomenon. From L. Schmelak, of Christiania, I have received a collection of beautifully crystalline Scandinavian minerals, containing some earths accompanied by more or less helium, but almost invariably nitrogen.

As instances he gives columbite, containing N, 0.067 per cent; yttritanite, with N, 0.0018; orthite, with N, 0.014.

Ammoniacal nitrogen has hitherto been rarely found in minerals. Its most common mineral source is carnallite. In this mineral the source of the carnallite is a maritime fauna which has perished. It is quite different with the ammoniacal nitrogen of the northern primitive rocks, which, according to the formation and deposition of such rocks, must be regarded as primitive nitrogen. This nitrogen will have been of the greatest importance for the origin of the vegetable world. At present almost the entire flora nourishes itself from animal nitrogen, which in a combined state goes through the well-known circulatory process. But how did the plant obtain combined nitrogen before there existed an animal world rich in nitrogen? The remarkable symbioses which enable the leguminosae to assimilate atmospheric nitrogen are evidently complicated phenomena of adaptation which cannot extend back to the origins of the vegetable world. For these commencements of plant-life it cannot have been indifferent that there were minerals—especially abundant in the North—where the atmospheric conditions were first suitable for the growth of plants; minerals which readily split off ammoniacal nitrogen under the influence of the atmosphere. At present agriculturists would do well to remember that there exists mineral nitrogen which, as the primitive stones weather, can be at once assimilated by all plants.—*Berichte*, xxix., p. 1710.

RAPID DETERMINATION OF
CARBONIC ACID IN THE AIR AND IN
CONFINED PLACES.

By M. HENRIET.

WE search for carbonic acid in the air and in confined localities by means of an arrangement which allows of a very rapid and very accurate determination. The reaction upon which we depend is the following:—

On adding sulphuric acid to a solution of neutral potassium carbonate, coloured red by means of a drop of phenolphthalein, the colouration disappears at the moment when half the carbonic acid of the carbonate is fixed upon the undecomposed carbonate, converting it into bicarbonate. This decolouration is very sharp if we take care, towards the end of the operation, to add the acid only drop by drop.

If we absorb in potassa the carbonic acid contained in a known volume of air, it is sufficient to titrate an equal

volume of the potassa liquid employed, when the difference of the readings multiplied by 2 corresponds exactly to the carbonic acid retained. We see that the result is independent of the carbonate which potassa liquid always contains, since in the liquid and in the carbonated liquid the pre-existing carbonate is decomposed by the same acid volume, and we take account merely of the difference of the readings.

Three experiments on artificial atmospheres of about 6 litres each gave the following figures:—

CO ₂ introduced. C.c.	Found. C.c.	Difference in fraction of volume.
2'400	2'430	$\frac{30}{1000}$
4'431	4'407	$\frac{24}{1000}$
5'596	5'594	$\frac{2}{1000}$

If we refer the gaseous volume to 100 cubic metres of air, we see that the error is—

For 40 litres CO ₂	..	0'5 litre.
" 74	"	.. 0'4 "
" 92	"	.. 0'0 "

It seems independent of the gaseous volume, and corresponds, in reading off the liquid poured out, to half a drop of the titrated liquid.

The specimen is taken in a flask of refractory glass containing about 6 litres, closed with a stopper of caoutchouc traversed by a bromine tube, penetrating into the neck of the flask by a few centimetres only, and by a second tube bent at right angles and fitted with a cock.

To take a sample of air we make a vacuum in the flask by means of a pump. We may further fill the flask with water, and empty it at the moment of taking the sample; but in this case it is proper, after having allowed the water to run away, to wash the flask with distilled water, and cause it to drain as completely as possible.

Whatever is the means adopted, when the flask has been stoppered we wait until the temperature within and without are in equilibrium. At this moment we close the cock of the elbow-tube and note the temperature.

When the flask is brought back to the laboratory we introduce into the bromine-tube 2 c.c. of ether and 15 c.c. of a pure solution of potassa (8 grms. per litre), the supernatant ether protecting the potassa against the carbonic acid of the external air. Whilst the flask cools in a current of water we introduce the potassa up to the stratum of ether. We repeatedly wash the bromine-tube with boiled water free from carbonic acid, introducing each time water into the flask. When the liquid, coloured more and more feebly by the phenolphthalein, becomes absolutely colourless, we agitate the liquid of the flask, giving it an oscillatory motion, which enables us to wet the sides of the neck. We let the contact continue for an hour, agitating at several intervals. The absorption is then complete.

We open the cock of the elbow-tube. The air escapes under a slight pressure. We then add the standard acid (1 c.c. of which is equivalent to 0'5 c.c. of carbonic acid) until the decolouration is complete, without fearing the influence of the carbonic acid of the external air, because the flask is full of decarbonated air.—*Comptes Rendus*, cxxiii., second half-year, p. 125.

AN IODOMETRIC METHOD FOR THE DETERMINATION OF CARBON DIOXIDE.*

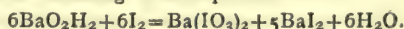
By I. K. PHELPS.

IN a recent paper from this laboratory (*Am. Journ. Sci.*, I., 101), it has been shown that carbon dioxide may be

estimated with accuracy by absorbing it under prescribed conditions in barium hydroxide, washing away the excess of the hydroxide, and converting the precipitated carbonate to the form of the sulphate. The chief difficulty in the process was occasioned by the fact that the barium carbonate precipitated from cold solutions is so finely divided and non-crystalline in character, that the removal of the excess of the hydroxide by filtration is a somewhat delicate and tedious process. The possibility of taking up by iodine the excess of the hydroxide remaining after the precipitation of the carbonate, and then determining the excess of iodine volumetrically, furnished the incentive to the following experiments.

The process, as finally developed, consists of three steps:—First, the evolution of the carbon dioxide and its collection in barium hydroxide contained in a partially evacuated flask; secondly, the conversion of the excess of the hydroxide to the form of iodide and iodate by adding an excess of iodine; and, thirdly, the titration of the excess of iodine with standard arsenious acid.

The barium hydroxide solution was prepared for use by filtering a cold saturated solution into a large bottle, from which it was drawn, or pumped, by means of the little improvised pump described by Kreider (*Am. Journ. Sci.*, I., 132); in either event care was taken to feed the air, which took the place in the bottle of the hydroxide removed, through potash bulbs to prevent the introduction of atmospheric carbon dioxide. The solution of barium hydroxide was standardised by drawing 80—90 c.m.³ of decinormal iodine into a glass flask, provided with a ground-glass stopper carrying an inlet tube reaching nearly to the bottom of the flask, and an outlet tube to which was sealed a Will and Varrentrapp absorption apparatus, and then introducing an appropriate amount of the barium hydroxide solution either from a burette or from a stoppered funnel which was weighed before and after. An ether wash-bottle answers admirably for a standardising flask, and with the glass stopper and its attachments replaced by a rubber stopper, answers the purpose of the absorption flask described later. The glass stopper is introduced, the inlet being closed by a rubber cap, and the absorption apparatus is charged with a solution of potassium iodide, to hinder the escape of iodine. The solution was brought to a boil, then cooled, and the excess of iodine determined by decinormal arsenious acid. It is assumed that the iodine lost acted on barium hydroxide according to the equation—



It was found necessary to boil the solution because of the formation of traces of the hypoiodite, which is broken up into iodide and iodate only by boiling, but which, if left unchanged, acts subsequently on the arsenious acid used in titrating the free iodine.

The apparatus which I have found most convenient for evolving the carbon dioxide from the carbonate consisted of a wide-mouthed flask of about 75 c.m.³ capacity, furnished with a doubly perforated stopper carrying a separating funnel for the introduction of acid into the flask, and a tube of 0'7 c.m. internal diameter, which is expanded to a small bulb just above the stopper, to carry off the gas. This exit tube was joined by a rubber connector to a tube which passed through the rubber stopper, closing the absorption flask (the ether wash-bottle used in standardising the barium hydroxide solution described above), and which ended in a valve preferably of the Kreider pattern (*loc. cit.*). This valve was enclosed in a larger tube reaching nearly to the bottom of the absorption flask. Through a second hole in the stopper of the absorption flask passed a glass tube closed by a rubber connector and screw pinch-cock.

In making a determination of carbon dioxide, the carbonate was introduced in weighed portions into the boiling flask. Barium hydroxide solution, in amount from 7—10 c.m.³ more than actually necessary to precipitate the carbon dioxide, was drawn into the absorption flask, which was

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. ii., Fourth Series, July, 1896.

then connected with the boiling flask, as described above. The stopcock of the separating funnel was shut off, and the flasks evacuated by connecting the exit tube of the absorption flask with a filter flask previously pumped out by the water pump, a mercury manometer registering the pressure. Exhaustion to a pressure of from 250–300 m.m. was found sufficient and easily attainable with the available water pressure in a minute's time. Sufficient phosphoric acid (chosen as a non-volatile acid) to dissolve the carbonate was introduced into the stoppered funnel with about 50 c.m.³ of water, which had been previously purified from carbon dioxide by boiling until one-third had been driven off in steam, and kept in full, stoppered flasks until used. The acid was then allowed to enter the boiling flask, and the carbon dioxide driven over completely to the absorption flask by boiling for five minutes—the latter being shaken frequently during the passage of the gas into it, and kept cool by standing in a dish of water. The atmospheric pressure was then restored by admitting purified air through the funnel of the boiling flask. In the experiments of Table I., the inlet tube of the absorption flask was closed by a rubber cap after disconnection, the exit tube was attached to potash bulbs, and the flask was cooled in a stream of water. The exit tube was removed, a capillary tube long enough to reach below the surface of the liquid introduced, and decinormal iodine run in until the large excess of barium hydroxide had been destroyed. Then the glass stopper of the absorption flask was introduced, with a rubber cap on the inlet tube and potassium iodide solution in the trap, as in standardising, and the emulsion brought to a boil. Iodine was again run into the hot solution through the inlet tube until the colour remained distinctly red after a second boiling. After cooling, the excess of iodine was determined by standard arsenious acid.

TABLE I.

	CaCO ₃ taken. Grm.	BaO ₂ H ₂ found. Grms.	BaO ₂ H ₂ found. Grm.	CO ₂ found. Grm.	Error. on CO ₂ . Grm.	Error. Corrected. Grm.
1.	0.0501	0.2484	0.1604	0.0227	0.0006+	0.0007+
2.	0.0500	0.2381	0.1508	0.0224	0.0004+	0.0005+
3.	0.1022	0.3416	0.1675	0.0447	0.0003–	0.0001–
4.	0.1026	0.3105	0.351	0.0450	0.0001–	0.0000
5.	0.2032	0.6181	0.2692	0.0896	0.0002+	0.0004+
6.	0.2049	0.5761	0.2223	0.0908	0.0006+	0.0008+
7.	0.5088	1.1301	0.2606	0.2232	0.0007–	0.0000
8.	0.5015	1.0804	0.2245	0.2197	0.0010–	0.0003–
9.	1.0032	2.0125	0.3004	0.4394	0.0020–	0.0006–
10.	1.0064	2.0702	0.3538	0.4405	0.0023–	0.0009–

In Experiments 7, 8, and 9, the barium hydroxide solution was estimated by weight—in the others by volume. The calcium carbonate used was Iceland spar in the form of chips, but, though it was the best material available and considerably better than the best commercial calcium carbonate at hand, the test of drying below red heat and the igniting to the condition of caustic lime with a blowpipe, proved it to be slightly deficient in carbon dioxide. The observed correction of 0.0014 gm. for each gm. of the carbonate is applied in the last column of the table.

The low results of the larger amounts of carbon dioxide, in contrast to the higher results of the smaller amounts, point to some action of the iodine upon the precipitated carbonate. It would be natural to suppose that such action would be greater upon the carbonate precipitated from a cold solution, and this proved to be the case. For when barium carbonate, precipitated under the conditions of the analysis described, was treated with 10 c.m.³ of iodine and boiled again, a loss of 0.0044 gm. of iodine (corresponding to 0.0008 gm. of dioxide) was found; but when barium carbonate was prepared by passing carbon dioxide through a cold solution of barium hydroxide until the presence of the acid carbonate was proved in solution by filtering a portion and boiling—thus insuring the complete destruction of the hydroxide—the precipitated carbonate, after filtering and washing, was

acted upon by 10 c.m.³ of iodine solution to such an extent that 0.0253 gm. of iodine (corresponding to 0.0044 gm. of carbon dioxide) disappeared. The obvious inference is, therefore, that the carbonate should be boiled before the addition of iodine in the process.

The experiments of Table II. were made like those of Table I., excepting in the following points:—First, an ordinary flask of about 300 c.m.³ capacity, which, fitted with a rubber stopper, was substituted for the more expensive ground stoppered absorption flask; secondly, the precipitated carbonate was boiled before adding any iodine; and thirdly, after iodine was added to a yellow colour and boiled, a second amount of iodine was run in to a red colour, but the mixture was not boiled again. By this treatment the iodine is kept from acting on the precipitated carbonate, at least to such an extent that the action is not appreciable, and from attacking the rubber stopper used; incidentally, it is kept from entering the trap, but one is used, nevertheless, to prevent contamination from the outside air. A separating funnel, reaching below the surface of the liquid, was found a convenient means of introducing the iodine without loss into the hot solution. A higher vacuum is required when the smaller flask is used, especially when large amounts of carbon dioxide are to be determined. A pressure of 200 m.m. of mercury was found to be sufficiently low, and in no case did a flask of ordinary thickness and of 300 c.m.³ capacity collapse at that degree of exhaustion.

TABLE II.

	CaCO ₃ taken. Grm.	BaO ₂ H ₂ taken. Grms.	BaO ₂ H ₂ found. Grm.	CO ₂ found. Grm.	Error on CO ₂ . Grm.	Corrected error. Grm.
1.	0.5023	1.1385	0.2851	0.2190	0.0020–	0.0000
2.	0.5056	1.1414	0.2801	0.2211	0.0014–	0.0006+
3.	1.0011	2.0712	0.3704	0.4367	0.0038–	0.0002+
4.	1.0030	1.8788	0.1736	0.4376	0.0037–	0.0003+

The calcium carbonate used in this test of the smaller apparatus was the purest commercial article available; the error applied as a correction in the last column (0.0040 gm. on carbon dioxide for a gm. of carbonate) was determined by five closely-agreeing analyses of various amounts in the larger apparatus.

The process, beside being delicate, is fairly rapid—the average time for a determination being about three-quarters of an hour.

It only remains to thank Prof. F. A. Gooch for many helpful suggestions and kindly advice in this investigation.

THE GRAVIMETRIC DETERMINATION OF SELENIUM.*

By A. W. PEIRCE.

THE method generally in use for the gravimetric determination of selenious acid is to precipitate the selenium with sulphurous acid in presence of hydrochloric acid and to weigh the elementary selenium. Precipitation by this method, however, is slow and incomplete in many cases, so that it is always necessary to treat the filtrate a second time with sulphurous acid and to digest for some time. To obviate the necessary delay in this process, I have tried the effect of substituting potassium iodide as the reducer instead of the sulphurous acid, adopting the idea from several recent volumetric methods for the determination of selenium† in which an iodide in acid solution is used to reduce the selenious acid, and in which the

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. i., June, 1896.

† Muthman and Schaefer, *Ber. d. Chem. Ges.*, xxvi., 1008; Gooch and Reynolds, *Am. Journ. Sci.*, i., 254; Gooch and Peirce, *Am. Journ. Sci.*, Fourth Series, i., 31.

liberated iodine, caught in various ways, is titrated and taken as a measure of the selenium.

Varying amounts of selenium dioxide, prepared according to the method described in former articles, by dissolving pure selenium in nitric acid, removing any selenic acid formed by barium hydroxide, and subliming in a current of dry oxygen, were dissolved in Erlenmeyer flasks, and the solution was acidified with hydrochloric acid; potassium iodide was added and the selenium was precipitated in the form of a red powder. Boiling for ten minutes served to reduce most of the liberated iodine and to change the selenium into the black modification, which was collected upon an asbestos felt, washed, dried at 100° to a constant weight, and weighed. Early experiments showed that for small amounts the process gave accurate results, but that for large amounts the errors came far too high:—

	Se taken. Grm.	Se found. Grm.	KI. Grms.	Volume. C.m.s.	Error. Grm.
1.	0.0355	0.0356	1	100	0.0001+
2.	0.0355	0.0355	1	100	0.0000
3.	0.0355	0.0356	1	100	0.0001+
4.	0.2968	0.3883	4	75	0.0915+
5.	0.2033	0.2475	4	100	0.0442+
6.	0.3058	0.3495	10	100	0.0437+

When the selenium amounted to less than a tenth of a gram, the results came out well. When the amount was larger the selenium assumed on boiling a pasty molten condition, which made filtering and washing impossible. This condition was observed in the work already referred to, and the mass seemed to consist of selenium with included iodine, as it gave up iodine slowly to water on standing, and more rapidly to a solution of potassium iodide.

It has been found in the work to be described that if an excess of potassium iodide be used considerably above the amount necessary for precipitation, the pasty condition of the selenium does not occur, the iodine evidently being held in solution by the excess of the potassium iodide. This would seem to indicate the total release of the iodine, and would make possible the determination of quantities larger than the two-tenths of a gram, set in the former work as a limit for the range of the process. Several determinations, which resulted very satisfactorily, were made according to the volumetric method thus modified, and at the same time the selenium which was precipitated was weighed. By the former method, in which the iodine evolved was estimated, the results were too low; and by the latter method, in which the residue was weighed, too high; but there appeared to be no definite relation between the errors of the two processes, as there would be if the retention of iodine were the only difficulty. Digestion of the selenium in the crucible with hot water removed a small amount of potassium iodide and reduced the error considerably; so that it was apparent that the increase in weight was due to the fact that the precipitated selenium included potassium iodide from the concentrated solution.

	SeO ₂ taken.	SeO ₂ found.	KI. Vol.	Error.	Se taken as SeO ₂ .	Se found.	Error.
	Grm.	Grm.	Grm.Cm.s.	Grm.	Grm.	Grm.	Grm.
7.	0.4870	0.4868	7 60	0.0002—	0.3467	0.3507	0.0040+
8.	0.4980	0.4971	10 60	0.0009—	0.3545	0.3575	0.0030+
9.	0.7323	0.7310	10 75	0.0013—	0.5214	0.5312	0.0098+

Later experiments under similar conditions, excepting that the volume of the liquid in which the precipitation took place was very much increased, so that the tendency on the part of the selenium to include the iodide might be diminished, gave errors entirely within satisfactory limits, though always positive. (See Table, next col.).

It is sufficient to dilute to 400 c.m.* before acidifying with hydrochloric acid and adding potassium iodide to an amount about 3 grms. in excess of that actually required. Boiling for ten to twenty minutes will change the selenium

	Se taken as SeO ₂ . Grm.	Se found. Grm.	KI. Grms.	Volume. C.m.s.	Error. Grm.
10.	0.2853	0.2861	7	900	0.0008+
11.	0.3189	0.3192	8	400	0.0003+
12.	0.3318	0.3324	7	500	0.0006+
13.	0.3798	0.3805	7	500	0.0007+
14.	0.4252	0.4259	7	350	0.0007+
15.	0.4430	0.4434	10	450	0.0004+

to the black modification and remove most of the iodine. The process of precipitation and filtering can be completed in half an hour. The selenium is dried at 100° to a constant weight.

When the selenium occurs in the higher form of oxidation the reduction follows the same course, though iodine is not liberated until the solution is quite warm; but at the end of the usual time of boiling the action is complete. The following shows the results obtained by acting in the manner described on selenic acid.

SeO ₃ taken.	Se taken. Grm.	Se found. Grm.	KI. Grms.	Volume. C.m.s.	Error. Grm.
0.1709	0.1063	0.1065	5	500	0.0002+
0.1709	0.1063	0.1062	5	375	0.0001—
0.3231	0.2010	0.2017	5	350	0.0007+
0.5005	0.3115	0.3126	6	500	0.0011+

Evidently this method will not distinguish between selenious and selenic acids, but it will be found of much value in point of time saved in the determination of either separately, or of the total selenium in case both occur together.

The kindly advice and suggestions of Prof. F. A. Gooch are gratefully acknowledged.

THE ACTION OF LIGHT ON SOME ORGANIC ACIDS IN THE PRESENCE OF URANIUM SALTS.*

By HENRY FAY.

(Continued from p. 57).

Determination of Uranium in the Brown Precipitate.

SOME of the freshly prepared substance was partially dried between filter-papers, transferred to a porcelain boat, and then dried at 100° in a stream of dry hydrogen. The substance, prepared in this way, has a pale, greyish green colour, resembling somewhat uranous oxalate, and in this condition shows very little tendency to pass over into the yellow substance. It was weighed rapidly, placed in a combustion-tube, and heated in a current of oxygen. When heated under these conditions the substance begins to glow, and the combustion spreads rapidly throughout the mass. After a very few minutes the substance is changed into the oxide U₃O₈. The boat is then withdrawn and weighed. The oxide obtained in this way is of a pale olive-green colour, and appears to be perfectly pure. The uranium was determined in six separate specimens in this way:—

I.	0.4768 gm.	gave 0.4407 gm.	U ₃ O ₈ = 78.47 p. c. U.
II.	0.2373	" 0.2180	" = 77.99 "
III.	0.1372	" 0.1249	" = 78.00 "
IV.	0.1556	" 0.1414	" = 77.15 "
V.	0.1856	" 0.1699	" = 77.58 "
VI.	0.1454	" 0.1314	" = 77.41 "
Average for the six determinations, 77.76 per cent U.			

* From the author's Thesis, submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy, June, 1895. The work was undertaken at the suggestion of Professor Remsen and carried on under his supervision. From the *American Chemical Journal*, xviii., No. 4.

These results, it will be seen, are fairly concordant, but good results could not be obtained for carbon.

Several attempts were made to determine the percentage of carbon, but, on account of the relatively small amount present, the results were not satisfactory. The substance, when heated alone, gives off small amounts of carbon monoxide, but, even by passing the gases over ignited copper oxide, good results were not obtained. The yellow substance, into which the brown one passes on standing, gave better results. These will be spoken of later. Various attempts were made to isolate the acid contained in this salt, but without success. The substance dissolves readily in hydrochloric, sulphuric, and nitric acids, forming green solutions, from which ammonia precipitates the black uranous hydroxide. All that can be said at present in regard to this salt is that it is a reduction product of uranyl oxalate. There can be no doubt that it contains a small percentage of carbon, as will be made more evident when the yellow transformation-product is considered. Ebelman believed it to be a hydrated oxide, but the presence of carbon proves this assumption to be wrong. Bolton obtained the same precipitate by exposing a solution of the double oxyfluoride of uranium and potassium acidified with oxalic acid. He however did not analyse the product. If this were the simple hydrated oxide, it seems that it should also be formed with other acids than oxalic acid, especially when the same salt of Bolton is acidified with formic acid. In this case only the salt $4UF + KF$ is formed.

Analysis of the Yellow Substance obtained from the Purplish-brown Precipitate.

The best way to prepare the yellow salt is to allow the brown substance to stand in a desiccator for four or five days. It is also formed when allowed to stand in the air, but it is more convenient to use the desiccator, as in this way the yellow salt can be obtained in dry condition having constant weight. For the analysis of this salt, it was dried to constant weight over sulphuric acid, or by heating in an air-bath to 100° . The substance is also formed when the brown precipitate is allowed to stand under water for several weeks. A preliminary test for carbon was made by heating the substance in a tube through which pure air was drawn. The gases were passed into barium hydroxide solution. There was considerable barium carbonate formed, showing carbon to be present.

This substance was heated in a combustion-tube as in the previous case, and the uranium oxide afterward weighed, the uranium, carbon, and hydrogen being thus estimated in the same operation. The substance was first converted into a brick-red substance, probably U_2O_5 , and on higher heating gave the oxide U_3O_8 .

Different preparations gave the following results on analysis:—

	U.	C.	H ₂ O.
I. 75.46 per cent.		1.36 per cent.	8.58 per cent.
II. 75.40 "		1.02 "	8.04 "
III. 75.10 "		1.2 "	8.50 "
IV. 74.9 "		1.15 "	8.7 "
V. 75.44 "		—	—

These results are selected from a much larger number of analyses, all of which agree very closely with the ones given.

It is difficult to account for the small amount of carbon present, but as none of the carbon was given off in the original decomposition, and the brown substance does not lose any carbon dioxide in drying, it is safe to say that all of the carbon is in combination with the uranium. In what form it exists it is impossible to say, as the substance dissolves in acid without separation of any organic acid. If all the uranium is precipitated and the filtrate separated, there is no evidence of any organic substance remaining behind.

Formation of Formic Acid in the Decomposition of Oxalic Acid.

Jones showed that the equation of Seekamp, representing the decomposition of oxalic acid by uranyl oxalate, does not express the reaction, as it does not account for the formic acid nor for the carbon monoxide. It was thought advisable to make a few experiments to see whether formic acid can be built up from carbon monoxide and water in presence of uranium salts. For this purpose the following experiments were made:—

I. A 250 c.c. Erlenmeyer flask was filled with a solution of uranyl oxalate, and about 100 c.c. carbon monoxide introduced into it. The inverted flask was connected with a long tube bent twice at right angles to show the pressure. The flask was exposed to the direct sunlight. Within two hours the decomposition of the uranyl oxalate was complete. The precipitate was the same as the one spoken of above when uranyl oxalate decomposes. No free acid was detected in the solution.

II. Carbon monoxide and water were exposed for fifteen days in the direct sunlight. On examination, at the end of this time, the water was perfectly neutral.

III. Mixtures of equal values of carbon monoxide and carbon dioxide, in the presence of water, were exposed to the direct sunlight, but no formic acid was obtained.

From these experiments it is shown that the formic acid obtained in the decomposition of oxalic acid is from the oxalic acid itself, and not from the combination of carbon monoxide and water.

Decomposition of Malonic Acid.

The study of malonic acid was next taken up, and it was my purpose to proceed as in the case of oxalic acid, but unexpected difficulties arose.

Uranyl malonate was prepared by bringing together hot concentrated solutions of malonic acid and uranyl nitrate. It separates in a few moments as a bright yellow crystalline powder, adhering firmly to the sides of the beaker. It is nearly insoluble in water and alcohol, more readily soluble in nitric acid, and easily soluble in a solution of malonic acid.

On analysis it gave the following results for uranium:—

Calculated for $CH_2 \begin{smallmatrix} COO \\ COO \end{smallmatrix} (UO_2) \cdot 3H_2O$, 56.06 p. c.

0.2526 grm. gave 0.1656 grm. $U_3O_8 = 55.65$ per cent U.

0.3682 " " 0.2416 " " = 55.70 " " U.

Heated to 110° for four hours it lost 9.15 per cent H_2O .

Calculated for $2H_2O$, 8.78.

At 180° , 0.2670 grm. lost in weight 0.0325 grm. = 12.16 per cent H_2O .

Calculated for $3H_2O$, 12.6 per cent H_2O .

This, like many uranium salts, loses some water readily, but loses the last molecule only at high temperatures.

As this salt is almost insoluble in water, it could not be used in this work. Accordingly, dilute solutions of uranyl nitrate and malonic acid were exposed to the light, but within a few minutes the uranyl malonate was completely precipitated. The uranyl malonate dissolves in potassium malonate, and it was hoped to use such a solution for the decomposition. The double salt of potassium and uranium was made by dissolving the uranium malonate in the required amount of potassium malonate. On evaporation well-formed, but small, very bright yellow crystals were obtained. Solutions of this salt, with and without free malonic acid, were exposed to the sunlight for several days, but there was no indication of decomposition in either case. They seemed to be perfectly stable in the brightest sunlight.

The same results were obtained when the uranyl malonate was dissolved in malonic acid and the solution exposed. The malonic acid decomposes when a dilute solution of uranyl oxalate and malonic acid is exposed to the sunlight, but the rate of decomposition is so extremely slow that it was not considered advisable at the time to carry the work further.

Decomposition of Succinic Acid.

Attempts were made to decompose succinic acid by means of uranyl succinate, but so far it has been impossible to effect such a decomposition.

Uranyl succinate is described in "Watts's Dictionary" as being made from uranyl nitrate and acid sodium succinate by evaporation to dryness. This method was tried, but the uranium salt obtained was so nearly insoluble in water that it was not suited for the experiments. Some of the salt obtained was dissolved in a dilute solution of succinic acid, and this solution exposed to the direct sunlight for some days showed no tendency to change. Various other methods were tried for the purpose of making uranyl succinate, but they were not successful. Solutions of uranyl nitrate and succinic acid can be evaporated to crystallisation, but they crystallise separately. It was also hoped to get it from barium succinate and uranyl sulphate. These salts were brought together in molecular proportions, but part of the barium was changed into sulphate and part into the insoluble barium uranate.

As it was desired to study the decomposition of succinic acid in the presence of uranyl succinate, the experiments were carried on further.

Seekamp (*Ann. Chem.*, Liebig, cxxxiii., 253) found that succinic acid decomposes in the sunlight, in the presence of uranyl nitrate, into carbon dioxide and propionic acid. This was verified qualitatively. The action takes place rather slowly, and, as this work could be carried on only during the winter and early spring months, it was not carried further. Seekamp believed the green precipitate in this case to be uranous succinate. A small amount of this substance was obtained and analysed for uranium, but the percentage did not agree with that required for uranous succinate.

It is necessary to do much more work on the precipitates obtained in these decompositions as they are difficult to obtain in a pure state, and, from analyses made of precipitates from other acids, they do not appear to be the simple reduction product.

Decomposition of Tartaric Acid.

When tartaric acid and uranyl nitrate are exposed to the sunlight, the clear yellow solution gradually turns to a deep green colour, and after a few hours there is a precipitation of a light green salt. No gas is given off in the reaction. Several solutions were attached to nitrometers containing mercury, but there was no change in the volume, although the solutions were under much reduced pressure. Heat facilitates the precipitation very greatly. Some of the green solution from which the precipitate had been removed was placed on a water-bath, when there was a complete precipitation in a few minutes. The precipitate is most readily formed when 1 molecule of uranyl nitrate is exposed with 1 molecule of tartaric acid. If the solution in which the precipitate has been formed is allowed to stand in the sunlight for several weeks, the green-coloured salt passes into solution, forming an amber-coloured liquid.

For analysis the green salt was dried between filter-paper and then over solid potassium hydroxide. It gave the following results:—

		I.	
0.2631 grm.	gave	0.1529 grm.	U ₃ O ₈
0.2631 "	"	0.0555 "	H ₂ O
0.2631 "	"	0.1396 "	CO ₂ .
		II.	
0.2949 grm.	gave	0.1713 grm.	U ₃ O ₈
0.2949 "	"	0.0684 "	H ₂ O
0.2949 "	"	0.1662 "	CO ₂ .
		Found.	
		Calculated for U ₆ H ₁₂ O ₁₆ .	
		I.	II.
Uranium ..	..	49.58	49.31
Hydrogen ..	..	2.48	2.34
Carbon ..	..	14.87	15.3

The nature of the above precipitate cannot be learned from the above results, and the formula suggested has no significance at present. It may be possible to isolate the organic portion of the salt, but until this has been done it would be useless to speculate in regard to the nature of the precipitate.

Decomposition of Isobutyric Acid.

Wisbar (*Ann. Chem.*, Liebig, cclxii., 232) has studied the action of sunlight on butyric acid in the presence of uranium salts, and found that it is decomposed into propane and carbon dioxide. It was thought desirable to know whether the other acids of this series undergo a similar decomposition, and accordingly a study was made of isobutyric, propionic, and acetic acids. The study of isobutyric acid was taken up first, as it was found to work readily, giving off gas freely when exposed to the sunlight with uranyl nitrate.

Experiments were first made to see whether any definite relations existed between the gases given off. Carbon dioxide was shown to be present by its ready absorption by potassium hydroxide, and the residual gas was burnt from the capillary tube of the nitrometer in which it was collected. It burned with a smoky flame, showing it to be a hydrocarbon.

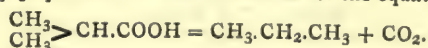
It was believed that the isobutyric acid would decompose in the same way as the butyric acid, giving equal volumes of propane and carbon dioxide. This was found to be the case, as is shown by the following experiment:—

I. For the purpose of collecting the gases the solutions were exposed in small test-tubes, 13 × 120 m.m., connected by means of a capillary tube to a nitrometer filled with mercury. The acid to be used was weighed directly into the tube, and a weighed portion of uranyl nitrate was added. Water was now added to bring the solution to the required height in the tube.

2.0201 grms. isobutyric acid and 0.3365 grm. uranyl nitrate were dissolved in 30 c.c. water and exposed to the sunlight. Gas begins to be given off about fifteen minutes after the exposure is made. After being exposed for nearly an hour the lower half of the solution becomes cloudy, and small drops of a dark green viscous liquid soon appear, which gradually collect in the bottom of the test-tube. Most of the gas evolved seems to come from this large drop. This dark green heavy liquid is, however, not always formed, and its formation depends on conditions which have not as yet been learned. A precipitate, however, is always formed—either this liquid or a light green powder.

The exposure was continued for several days when all action ceased. All of the uranium was precipitated.

The total volume of gas was 30 c.c., and of this 14.8 c.c. were absorbed by caustic potash, which shows half the volume of gas to be carbon dioxide. This also shows that the total decomposition of the acid was approximately 30 per cent of that calculated for the equation—



At the end of the first day's exposure 21.5 per cent of the decomposition had taken place.

II. This experiment was carried on precisely as the preceding, except that, after the reaction had begun, a tube filled with warm water was placed around the tube containing the solution. This increased the reaction very much, and it was found that by this method large quantities of the gases can be collected in a very short time. Of 27 c.c. gas collected, 13.6 c.c. were absorbed by caustic potash.

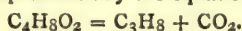
III. In this experiment much larger quantities of acid and uranyl nitrate were used for the purpose of securing a pure specimen of the hydrocarbon for analysis. After 25 c.c. of the gas had been collected, it was removed from the nitrometer, so as to get rid of any oxygen or nitrogen possibly held in solution by the water. This was repeated

several times before a sample of the gas was collected for analysis.

The gas was removed by having it under pressure by means of the pressure-tube connected with the nitrometer, and then opening the glass stopcock of the nitrometer only a little way. The stopcock was closed before all of the gas had escaped, thus making sure that no air could enter. By this means it was found possible to collect the evolved gas. On absorption, exactly half of the volume was shown to be carbon dioxide. The remaining portion was then transferred to a eudiometer and exploded with oxygen.

Volume of original gas 21.3 m.m. = 1 vol.
Volume after addition of oxygen 400.7 .. = 18.81 vols.
Volume after explosion 335.9 .. = 15.76
Contraction = 3.05 ..

The calculated contraction for C_3H_8 is 3 volumes. This shows the hydrocarbon to be propane, and the reaction is to be represented by the equation—



Decomposition of Propionic Acid.

Uranyl nitrate and propionic acid, when exposed to sunlight, decompose very readily, giving off gas in a few minutes after exposure is made. It was found best to use a rather strong solution of the acid. The gas is given off evenly, and continues until nearly all of the acid is decomposed. The gas was collected and analysed in the same manner as described under isobutyric acid.

I. 32.4 c.c. of gas gave .. 15.8 c.c. CO_2 .
II. 30.5 15.1 ..
III. 26.4 13.2 ..

These figures show that approximately half the volume of the gas is carbon dioxide.

The residual portion was run into a eudiometer and exploded with oxygen.

Volume of original gas 19.97 m.m. = 1 vol.
Volume after addition of oxygen 201.12 .. = 10.07 vols.
Volume after explosion 147.44 .. = 7.38
Contraction = 2.69 ..
Calculated contraction for C_2H_6 = 2.5 ..

This shows the hydrocarbon to be ethane, and the decomposition of propionic acid is to be represented by the equation—



(To be continued).

OXIDATION OF SODIUM SULPHIDE AND HYDROSULPHIDE TO THE SULPHATE BY ELECTROLYSIS.*

By FRANK W. DURKEE.

It is very well known that potassium and sodium chlorates can be made from the chlorides in solution by electrolysis, and various other substances oxidised by the same means. Sodium sulphate mixed with acid sodium hydrosulphite, $NaHS_2O_4$, has been produced from acid sodium sulphite (E. H. Ekker, *Rec. Trav. Chim.*, xiv., 57-64, 1895), but I am not aware that any one before has attempted to make sulphates from the alkaline sulphides and hydrosulphides by electrolysis. At the request of Mr. F. S. Pearson, Engineer of the Metropolitan Traction Company of New York City, experiments were begun to show whether or not it would be possible to transform the ammonium compounds in gas liquors directly into sulphate of ammonium by use of the electric current. In the preliminary experiments, gas carbon electrodes were used, and ammoniacal

sulphide and hydrosulphide solutions, but with this arrangement the three-ampère current, which passed through the solution for several hours, failed to produce any sulphate. The sulphide solution was blackened, however, by the finely divided particles of carbon which separated from the electrodes. Copper electrodes, when used in place of the carbon, were soon covered with copper sulphide, and the ammonium sulphur compounds were not oxidised. The oxidation went on very well when platinum electrodes were used, and ammonium sulphate in considerable quantity was produced. Solutions of sodium hydrosulphide and sodium sulphide were then subjected to electrolysis, and sulphate of sodium obtained. These experiments, however, were not conducted in a way to show that all of the alkaline metals in the compounds present could be changed to sulphate by electrolysis. This point seemed of so much importance that an attempt was made to settle it, first of all, at the beginning of the investigation, and in the following way:—

Fifty c.c. of a solution of sodium hydroxide, prepared from sodium and distilled water, were measured out into a small flask, and supersaturated with hydrogen sulphide. An equal volume of the same solution of sodium hydroxide was then added, and the resulting solution, approximating a sulphide, was poured into a tall beaker of about one litre capacity. 300 c.c. of water were added. To prevent loss by spattering during the process of electrolysis, the beaker was covered with a watch-glass, notched to admit the wires which extended to the electrodes. The electrodes themselves, of thick platinum foil, were cylindrical in form, three inches long and one inch in diameter. Heavy platinum wires connected the electrodes to the battery circuit. When in use, the electrodes were thrust nearly to the bottom of the beaker, were parallel, and one and a-half inches apart. After proper connections had been made with a storage battery, a current of about 3.1 amperes flowed through the liquid for about eleven hours and thirty-five minutes. Then the circuit was broken and the solid matter, mostly sulphur, filtered out. Afterwards enough water was added to the filtrate to make 1000 c.c. A second solution was then prepared in exactly the same way as the first and made up to 1000 c.c.

It followed, therefore, that 1 c.c. of the new solution contained as much sodium as 0.1 c.c. of the original solution of sodium hydroxide, and 25 c.c. as much as 2.5 c.c. of the solution of hydroxide. If, then, pains be taken to determine accurately the weight of sodium combined as sulphate in 25 c.c. of the solution after electrolysis, it should exactly equal the weight of the sodium in 2.5 c.c. of the solution of hydroxide, if the oxidation to sulphate by electrolysis is complete and quantitative. Tested qualitatively, the solutions were neutral and gave the reactions only of sodium sulphate. Consequently, to get the weight of sodium sulphate, it is only necessary to evaporate to dryness in a weighed platinum crucible, on a water-bath, 25 c.c. of the solutions after electrolysis, heat and weigh. The weight of the sodium could then be calculated from the weight of sodium sulphate found. Duplicate determinations of sodium sulphate were made in each solution, and the results are below.

Solution No. I.

- Weight of Na_2SO_4 in 25 c.c., 0.2641 grm.
- Weight of Na_2SO_4 in 25 c.c., 0.2653 grm.

Weight of Na calculated from an average of weights of Na_2SO_4 obtained in the above determination, 0.0857 grm.

Solution No. II.

- Weight of Na_2SO_4 in 25 c.c., 0.2636 grm.
- Weight of Na_2SO_4 in 25 c.c., 0.2638 grm.

Weight of Na calculated from an average of the weights of Na_2SO_4 obtained in the above determinations, 0.0854 grm.

To determine the effects of the electric current upon solutions of hydrosulphide of sodium, 100 c.c. of the solu-

tion of sodium hydroxide were supersaturated with hydrogen sulphide, diluted to 400 c.c. by addition of water, and treated for about eleven hours with a three-ampère current. Considerable sulphur separated. This was filtered off and enough water added to make 1000 c.c. During the electrolysis some of the sulphur was oxidised to sulphuric acid, as was shown, both by the use of blue litmus paper and by a quantitative determination with barium chloride in hydrochloric acid solution. In all, two solutions, like the one just described, were prepared and analysed as before, with the following results:—

Solution No. I.

- a. Weight of Na_2SO_4 in 25 c.c., 0.2648 grm.
- b. Weight of Na_2SO_4 in 25 c.c., 0.2638 grm.

Weight of sodium calculated from an average of the weights, Na_2SO_4 obtained in the above determinations, 0.08545 grm.

Solution No. II.

- a. Weight of Na_2SO_4 in 25 c.c., 0.2636 grm.
- b. Weight of Na_2SO_4 in 25 c.c., 0.2640 grm.

Weight of sodium calculated from an average of the weights of Na_2SO_4 obtained in the above determinations, 0.08545 grm.

Determined by standard acid, the sodium in 2.5 c.c. solution of sodium hydroxide was 0.0860 grm. The sulphate method gave, as an average of duplicate determinations, 0.0858 grm. and the average of 0.0860 grm. and 0.0858 grm. is 0.0859 grm., the weight of sodium in 2.5 c.c. of the solution of sodium hydroxide.

This weight, 0.0859 grm., should correspond to the weight of sodium in 25 c.c. of the solution after electrolysis, if the oxidation of the sulphur compounds to sulphate is complete. For the sake of a better opportunity for comparison, the figures already obtained by analysis have been inserted below in a group.

Sodium in 2.5 c.c. NaOH solution, 0.0859 grm.

Solution of Na_2S after Electrolysis.

- Sodium in 25 c.c. of No. I., 0.0857 grm.
- Sodium in 25 c.c. of No. II., 0.0854 grm.

Solution of NaSH after Electrolysis.

- Sodium in 22 c.c. of No. I., 0.08545 grm.
- Sodium in 25 c.c. of No. II., 0.08545 grm.

While the weights of sodium found in 25 c.c. of the solutions after electrolysis do not exactly agree with the weight found in 2.5 c.c. of the solution of sodium hydroxide, the agreement is so close that the complete change of sulphide and hydrosulphide to sulphate by electrolysis seems certain.

By what chemical change or changes is sulphate of sodium produced from sodium sulphide electrolytically? During the electrolysis of sulphide solutions, in the apparatus before described, some information on this point has been obtained by inspection. As soon as the current began its work electrolytic hydrogen escaped rapidly from the solution about the negative electrode. On the other hand, very little oxygen escaped at the positive. After the current had passed for a short time, the solutions, nearly colourless at first, grew yellow about the negative electrode, and the yellow colour rapidly diffused throughout the electrolyte. Later light yellow sulphur made its appearance on the positive electrode. It scaled off, however, as the electrolytic process proceeded, and the greater part dissolved in the surrounding liquid. Next, in order, fine white sulphur separated in little clouds about the positive electrode, near the surface of the liquid, but dissolved completely as it sank toward the bottom of the beaker cell. With the continuation of the electrolytic process, the clouds of fine white sulphur became larger and denser, so that immediately before the yellow colour disappeared from the electrolyte altogether, they did not dissolve, but gradually diffused

throughout the liquid and finally settled down upon the bottom of the beaker. At this stage of the electrolysis, and a little later, much more oxygen escaped from the solution than at any previous time during the passage of the electric current. The solutions were gradually warmed by the electrolytic action.

Taken up in reverse order, the phenomena above described are to be interpreted as follows:—The fine white sulphur separating in little clouds about the positive electrode, shows that sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, is present and being oxidised to sulphate in the electrolyte, while the light yellow sulphur, which adheres at first to the positive electrode, indicates the presence of polysulphides. These assertions rest upon the data collected during the electrolysis of sodium polysulphide and thiosulphate solutions in the apparatus already described. By such experiments it has been found that the sulphur from a thiosulphate solution always comes down finely divided and white, and does not adhere closely to the positive electrode. In a polysulphide solution, on the other hand, it clings tightly to the positive electrode at first, later scales off, and is light yellow in colour. The yellow colour of the electrolyte also indicates the presence of polysulphides. Again, after filtering off the precipitate formed by adding excess of ammoniacal zinc solution, the filtrate always gives the reactions of thiosulphate, on addition of an acid, provided the electrolysis is broken off after the little clouds of white sulphur begin to separate. The oxidation of sodium sulphide and hydrosulphide to sulphate is complete when the white sulphur separates no longer at the positive electrode. As for the electrolytic hydrogen, since it escapes from the electrolyte, it could not have acted chemically upon any substance therein. Moreover, if it had acted chemically, it must have acted as a reducing agent, in which event, from the nature of the substances in the liquid, sulphur would probably have separated at the negative electrode instead of the positive, just as it does in the electrolysis of aqueous solutions of sulphur dioxide, or would have combined with the liberated hydrogen to form hydrogen sulphide. But nothing of the sort happens. On the other hand, since electrolytic oxygen does not escape from the electrolyte, at least not during the first stages of the electrolysis, it must combine chemically to oxidise some substance or substances in the solution. It would seem very probable, therefore, that the oxidation of sodium sulphide and hydrosulphide to the sulphate is not retarded to any extent, at least, by the presence of electrolytic hydrogen, in which event the oxidation might be expected to go on, except so far as rate is concerned, in very much the same way that it does when air is drawn through solutions of sodium sulphide.

(To be continued).

NOTICES OF BOOKS.

Elementary Practical Chemistry and Qualitative Analysis.

By FRANK CLOWES, D.Sc., F.I.C., Professor of Chemistry in the University College, Nottingham, and J. BERNARD COLEMAN, A.R.C.Sc., F.I.C., Head of the Chemical Department, South-West London Polytechnic. London: J. and A. Churchill. 1896. Post 8vo., pp. 224.

THE work before us, as we are informed in the authors' preface, is founded on a larger treatise on qualitative analysis with the addition of a special section experimentally illustrating the leading principles of chemical science.

The work commences with a list of apparatus required for each work-table in the laboratory of a college, the preparation and uses of apparatus, experiments showing the preparation of some gases and liquids, chemical

operations shown experimentally, and experiments involving weight and measurement.

Then follow analytical reactions. The reactions for metals, arranged in the usual groups; the reactions for acid radicles; the analysis of simple substances containing only one metal and one acid radicle; and a full analytical course with tables.

The appendix contains a list of chemical elements, atomic weights, equivalent weights, thermometric scales, weights and measures, and a list of formulæ.

This book, along with many others, may well be termed good seed, but when may we expect to reap the harvest, instead of importing it from Germany?

The Derivatives of Naphthalin which possess Technical Interest, arranged as a Conspectus. ("Die Derivate des Naphthalins welche für die Technik Interesse, besitzen übersichtlich zusammengestellt.") By ERNST TAÜBER and RAGNAR NORMAN. Berlin: R. Gaertner's, Publishers. 1896. Pp. 219.

THE German scientific press does not, like our own, overflow with manuals and epitomes each of which bears a strong family likeness to the rest. But in return it is rich in monographs and in original works of well-marked technical value.

The appreciation of theory met with on the other side of the North Sea has more than justified itself in practice.

The contents of the work before us have appeared in the *Chemische Industrie*, and then as an independent pamphlet.

The authors treat successively of the amidonaphthalinesulpho acids, and of the oxynaphthalinesulpho acids, the diamidonaphthalines, the diamidonaphthalinesulpho acids, the dioxynaphthalines and their sulpho acids, the amido-oxynaphthalines and their sulpho acids. To each of these sections is added a copious appendix.

Then follows a view of the literature of the subject, giving in parallel columns the name of the inventor, the journal in which the original work appeared, and the chief abstracts. Next we have a tabular view of the di- and tri-, the naphthalindi-, tri- and tetra-sulpho acids, the mononitronaphthalin, mono-, di- and trisulpho acids of known constitution.

Then follows an alphabetical list of those commercial or "trivial" names which do not indicate to what group the compounds in question belong.

In an appendix we have a list of publications which appeared whilst the body of the work has been printed.

Lastly comes a list of applications for patents which have been accepted; another list of those for which protection has been refused; and another list of such as have in the meantime expired.

Concerning the value of this work it is almost superfluous to speak. To chemists concerned with the manufacture, the use, or the investigation of the artificial colours, it will be found of the utmost utility.

A Short History of the City and Guilds of London Institute for the Advancement of Technical Education. London: City and Guilds of London Institute. 1896.

FROM this pithy pamphlet we learn that the first step towards the formation of the City and Guilds of London Institute took place not less than twenty years ago, the main object being "to educate young artizans and others in the scientific and artistic branches of their trades."

The next year a provisional committee was formed, and it was resolved that the object in view would best be attained by the establishment of a Central College for the advanced education of such as had already acquired a sufficient knowledge of science or the arts to enable them to profit by the instruction in the industrial applications

of these; secondly, by conducting examinations (!) in technological subjects; and thirdly, by the establishment of local schools for artizans and workmen. Mention was made, as a model to be aimed at, of the Federal Polytechnic School of Zurich.

The Presidents of the Royal Society, and of the Chemical Society, of the Institution of Civil Engineers, and the Society of Arts are recognised as *ex officio* members of the Institute and its managing committees. The number of day-students at the Central College is now 208, and of evening students 526.

The Technical College at Finsbury—a much more suitable locality than South Kensington—is also flourishing. The chair of Electrical Engineering is filled by Prof. S. P. Thompson, D.Sc., F.R.S., and that of Chemistry by Prof. P. Meldola, F.R.S. The day students number 210, and the evening students 926.

The amount subscribed by the Companies to these Institutions during the past eighteen years has been £480,800. We believe that, as regards our national industries, this is a much better investment than the millions swallowed by the School Boards. A glance at a Financial Table may edify those who think that the City Guilds spend their means in a series of dinners.

Beginners' Guide to Photography, showing how to Buy a Camera and how to Use it. By A FELLOW OF THE CHEMICAL SOCIETY. Published by Perken, Son, and Rayment, 97, Hatton Garden, London, E.C.

HERE, in the compass of 217 pages, we have an excellent guide for all who are taking up photography, clear, simple, and yet sufficiently comprehensive. We are particularly gratified with the section on micro-photography, a branch of the subject which, so to speak, is too often allowed to fall to the ground between two stools.

The learner will find here all which can be obtained by verbal tuition; experience and observation must do the rest.

Chemistry at a Glance: a Study in Molecular Architecture. By HERBERT B. TUTTLE. New York. 1896.

UNDER this title we have the first part of an elementary work on chemistry, treating exclusively on oxides, and running to the extent of 60 pages; other parts being to follow. We are of course unable to say whether a person ignorant of chemistry would, by a glance at this work, acquire a clearer and fuller knowledge of chemistry than he could by other means.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 2, July 13, 1896.

Evaporation of Metals at the ordinary Temperature.—H. Pellat.—With reference to M. Colson's communication (p. 49 of the current volume) on the "Action of Zinc on a Gelatino-Bromide Plate," the author mentions that he obtained quite similar results with steel four years ago. He ascribed these results to the influence of a metal upon the nature of the surface of another metal placed at a little distance (*Comptes Rendus*, xciv., p. 1247).

Process for Photographing Objects in Relief and Depression, and vice versa.—Ernest Moussard.—The author takes an impression of the object by moulding in plaster or paper, and photographs this impression, which

is the inverse of the original, taking care to place at the bottom the top of the mould to be photographed, putting in the frame the gelatino-bromide plate, with the glass above and the sensitive layer below, so as to obtain a negative proof of the mould, which is itself the negative of the object, and then operate as usual.

Manner in which the X Rays occasion the Discharge of Electrified Substances.—Emilio Villari.

Action of Metallic Tubes and Discs upon the X Rays.—Emilio Villari.—The action of the rays which strike the electroscope is not transmitted by the wire to the aluminium disc. In the case of a leaden disc struck by the rays on its paraffined side the discharge from the uncovered side can only be produced by the rays which turn round the edge of the disc and penetrate into its shadow.

Action of the Röntgen Rays upon the Bacillus of Diphtheria.—F. Berton.—The author has exposed cultures of the bacillus of diphtheria in broth to the Röntgen rays for 16, 32, and 64 hours. After each exposure the cultures were sown in broth and injected into guinea-pigs. A check culture was similarly re-sown and injected into two guinea-pigs. The results were negative. The animals died as rapidly in the one case as in the other. This result agrees with that obtained by Wade (*British Med. Journal*) and Minck (*Mün. Med. Wochenschrift*).

Fusibility of Metallic Alloys.—Henri Gautier.—The researches of Le Chatelier show the absolute identity of alloys with the mixture of a salt and of water, commonly known as solutions. The curves of solubility correspond to the curves of fusibility. Metallic alloys are bodies whose crystalline structure is perfectly recognised. Thus the alloys of tin with zinc, bismuth, and lead correspond to the case where no combination ensues. The alloys of copper with tin and antimony correspond, on the contrary, to the case of a combination. The author points out an error which has been reproduced in all chemical text-books. The fusion-point of antimony is given as near 430° , whilst in reality this metal melts only at redness; its point of fusion determined by the pyrometer is 632° .

On Steel Diamonds.—M. Rossel.—This paper requires the four accompanying figures. It seems to the author that the formation of diamonds by the absorption of carbon by iron at a very high temperature and crystallising out as diamond when cooling under high pressure receives a new confirmation, and the theory of the production of diamonds put forward by M. Moissan appears to us perfectly justified.

Action of Silicon upon the Alkaline Metals, Zinc, Aluminium, Lead, Tin, Antimony, Bismuth, Gold, and Platinum.—Emile Vigoureux.—From the point of view of their behaviour with silicon we may divide the metals into two groups: those which do not combine directly with this element and those which do thus combine. We may include in the former class the alkaline metals, zinc, aluminium, lead, tin, antimony, bismuth, gold, and silver. They dissolve it almost all more or less abundantly, and abandon it afterwards in the form of crystals. The metals capable of uniting directly with silicon to form silicides perfectly crystalline are iron, chromium, nickel, cobalt, manganese, copper, and platinum. The composition of iron silicide (SiFe_2) and of chromium silicide (SiCr_2) having been first established by Moissan I have afterwards recognised that for all crystalline silicides it is analogous, i.e., SiM_4 (M being a monatomic metal). A certain number of these new compounds dissolve silicon, as do the metals, e.g., copper silicide, platinum silicide.

On the Double Cyanides.—Raoul Varet.—These results and those obtained with mercury cyanide show that the double salts formed by the metallic cyanides properly so-called, on combining with the cyanides of the alkaline and alkaline earthy metals, have the same formation heat in the dissolved state when we consider one

and the same group of salts. They cannot be dissociated by dialysis. These characters permit us to consider them as derivatives of acids which do not exist in the free state or are at least very unstable, like the argentocyanhydric acid. The different double cyanides are distinguished from each other less by the difference of their molecular arrangement than by their greater or less stability.

Action of Water upon Formic Aldehyd. Application to the rôle of this Substance in Plants.—Marcel Delépine.—The facts established seem worthy of excessive interest if we only reflect that formic aldehyd is considered as the first term of the assimilation of carbon by chlorophyllic vegetables. If we suppose that the above reactions effected chemically at high temperatures take place physiologically in the plant at ordinary temperatures we may deduce numerous consequences. To the transformations of methylic aldehyd already admitted we must add a new one, enabling us to conceive why this compound is so difficult to detect, being liable to multiform transformations. By its splitting up into formic acid and methylic alcohol we may explain the presence of these two bodies in plants. We see, further, how formic acid may exist free, being formed by the action of water without the presence of a base being necessary. By its decomposition into carbonic acid and methylic alcohol we see that the presence of the latter almost universal in green leaves is not necessarily correlative with that of formic acid. But the most important consequence is the supply of an excess of hydrogen with elimination of carbonic acid.

Reduction of Crotonic Aldehyd.—E. Charon.—This paper is not well suited for abstraction.

Rapid Determination of Carbonic Acid in the Air and in Confined Places.—M. Henriet.—(See p. 64).

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxiv., No. 2.

Use of Thioacetic Acid in Analysis in place of Hydrogen Sulphide.—MM. Schiff and Tarugi.—To effect a precipitation, we add the reagent to the solution of the metals in hydrochloric acid. We heat on the water-bath, keeping below the point of ebullition. The precipitate is collected after the liquid is cold. The following is the action of ammonium thioacetate on the most important metallic salts. From $1\frac{1}{2}$ to 2 c.c. of the reagent are generally sufficient to precipitate 0.5 to 1 grm. of a metallic salt.

Arsenic.—In the cold a whitish turbidity; in heat the arsenites and arseniates give a precipitate of arsenious sulphide.

Bismuth, Copper, Tin.—The salts of these metals are partially precipitated in cold, completely in heat.

Lead.—In the cold a deep red precipitate (chloro-sulphide?), which is converted totally into black sulphide on heating.

Silver.—A black precipitate. Silver chloride dissolved in hot hydrochloric acid is completely converted into sulphide.

Cadmium.—The precipitation is often not complete until after cooling.

Mercury.—Mercuric salts behave like those of lead.

Platinum.—In the cold a red precipitate of indefinite composition, which is converted into sulphide if heated.

Gold.—Like platinum.

Iron.—Ferric salts are at once reduced to the ferrous state, when the action ceases.

Chrome.—The chromates are reduced to the state of chromic salts, upon which the thioacetate has no action.

Aluminium, Manganese, Zinc, Nickel, Cobalt.—The salts of these metals are not precipitated by the acetate in an acid solution.

No. 3.

Chemical Analysis and Bacteriological Examination of Potable Waters.—W. J. Mason.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. i., No. 5.

The only chemical matter contained in this issue is a memoir on the improvements recently introduced in the beet-sugar industry.

No. 6.

Report by M. Aimé Girard on the Control of Agricultural Distilleries, as proposed by M. Sidersky. — M. Sidersky, it appears, has been appointed a permanent inspector of the agricultural distilleries. There was considerable jealousy at his appointment, but the arrangement has been found to work well in practice. We should suggest, however, that such inspectors should, in case of resignation, be bound most stringently not to act as consulting experts in this department of chemistry. It is here mentioned that the work effected by M. Sidersky during the first two years of the commission entrusted to him are full of interest from a professional point of view.

Report submitted by M. de Luynes on behalf of the Committee of Chemical Arts on M. Lefèvre's Treatise on Colouring Matters. — This work, which supplies a serious deficiency in French chemico-technical literature, is divided into twenty chapters, each referring to a class of colouring matters. After expounding Witt's theory of chromospheres and chromogenes the author treats of the nitro- and azoxy-colours. Chapter III. comprises the study of the azo-colours, along with which are arranged the sulphone compounds of the amines, the phenols, and the amido-phenols. The chapter concludes with a complete table of the azo-colours hitherto known, and with an indication of colours on the fibre. There are here found figures showing the plant required in the manufacture of the azo-colours. In the other chapters of the first volume we find described with equal care all that pertains to the hydrazinic colours, the indamines, the indones, the oxindamines, the oxindones, the thiazines, the eurhodines, the safranines, and the indulines. The colours discussed in the second volume are all derived from the subjoined carbides, except the colours derived from the chinoleic bases. They are the colours derived from naphthalene, diphenylmethane and its homologues, triphenylmethane and its homologues, anthracene and its homologues. The last chapter but one is devoted to the artificial indigos. In short, this work, of more than 1600 pages, contains all that has been done or published on the artificial colouring matters.

Report presented by M. Schützenberger on behalf of the Committee of Chemical Arts on G. Segny's Ozoniser. — This apparatus is intended for the application of ozone for industrial, medical, and antiseptic uses. The condensation is effected by means of the electric effluve. The apparatus consists of three wide horizontal tubes of glass connected so as to form a single tube traversed by air or oxygen.

MISCELLANEOUS.

Oil of Reseda Root. — J. Bertram and H. Walbaum (*Journ. Prakt. Chemie*). — This oil is light brown, smells distinctly of horseradish, and boils under ordinary pressure at 255° with decomposition. Its specific gravity at 15° is 1.067. It is slightly dextro-rotatory.

Examination of Crude Olive Oil. — E. Dietrich (*Helfenberger Annalen*). — The oil often contains much stearic acid and almost always fluctuating proportions of glycerides. The former constituent is ascertained by the acid number and iodine number, and the latter by the saponification number.

Brazilian and Carolina Monazite. — Carolina monazite occurs in irregular crystals, some being as large as a grain of wheat, and requires crushing, for which reasons the Auer-Welsbach Company, of Berlin and Vienna, pre-

fers the Brazilian monazite which comes in the form of a fine sea-washed sand. A ton of Brazilian monazite sand, costing at present in Hamburg 119 dols., yields, when well worked out, from 20 to 25 kg. of pure thoria, which is worth from 2400 dols. to 3000 dols., according to degree of purity. Thorium oxide is now worth in Germany from 120 dols. to 150 dols. per kilogram., according to purity, and Mr. Mason, Consul at Frankfort, suggests the establishment in the monazite region of this country of a laboratory "where by employing the most improved and economical methods, the monazite, including the poorer sands which have been concentrated by a process recently perfected, may be worked up, the thoria extracted and made available as a finished product in all countries where incandescent gas burners are manufactured." — *Engineering and Mining Journal*.

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1916.

THE HOMOGENEITY OF ARGON AND OF HELIUM.

By Prof. W. RAMSAY and J. NORMAN COLLIE.

THE question of the homogeneity of argon has been discussed by Lord Rayleigh and one of us in their memoir on Argon (*Phil. Trans.*, A, p. 236, 1895). But at that epoch the data were not sufficiently numerous to enable us to arrive at very definite conclusions. The discovery of helium and the analysis of its spectrum by Runge and Paschen (*Sitzungsberichte d. Akad. d. Wissenschaften*, pp. 639 and 759, Berlin, 1895) lead to the thought that this body may be a mixture of two gases.

To elucidate this question we submitted these two gases to a methodical diffusion, causing them to traverse a duct of porous pipe-clay submitted on one of its surfaces to the action of a vacuum. We satisfied ourselves that we might thus effect the separation of hydrogen and helium and that of oxygen and carbonic acid, and that, by measuring the rapidity of the descent of a column of mercury introduced in the circuit of the apparatus, it is possible to arrive at a good determination of the molecular weight of various gases. We have then tried to separate argon into two parts by a method analogous to the separation of liquids by fractionated distillation.

The quantity of argon was close upon 400 c.c. The gas was then treated in the manner shown in the following scheme:—

More diffusible.		I.		Less diffusible.	
	$\frac{1}{2}$	..	..	..	$\frac{1}{2}$
II.	$\left\{ \begin{array}{l} \frac{3}{4} \\ \frac{1}{4} \end{array} \right.$	..	..	$\frac{1}{4}$	$\frac{3}{4}$
III.	$\left\{ \begin{array}{l} \frac{3}{4} \\ \frac{1}{4} \end{array} \right.$	..	..	$\frac{1}{4}$	$\frac{3}{4}$
IV.	$\left\{ \begin{array}{l} \frac{3}{4} \\ \frac{1}{4} \end{array} \right.$	..	..	$\frac{1}{4}$	$\frac{3}{4}$

We determined the density of the two extreme portions, and found that the one which ought to be the lightest had the density ($O=10$) of 1.93, and the heaviest of 2.01. The separation, if it takes place, is therefore minimal.

The same experiment executed with helium yielded other results. The density of the specimen which passed first was 1.874, and that of the gas remaining in the apparatus 2.133. A great number of fractionations did not change these figures; even the spectra of the two specimens were absolutely identical. Even the first bubbles of the lighter gas showed the same lines, with the same intensity, as the last bubbles which remained in the apparatus. There was no difference in fifty fractions.

Lord Rayleigh has had the kindness to measure the refraction of the two specimens of gas. Whilst the lighter gives the figure 0.1350 (atmospheric air = 1), the heavier had a refraction expressed by the figure 0.1524. Now these two numbers have a relation almost identical with the relation of the densities, for—

$$\frac{0.1350}{0.1524} = \frac{1.874}{2.110} \text{ in place of } \frac{1.874}{2.133}$$

Let us now consider what happens when we submit a mixture of the two gases to diffusion. Let us take, e.g., a mixture of hydrogen with an excess of oxygen. After a sufficient number of operations we obtain pure oxygen on the one hand, and on the other a mixture of 1 part of

hydrogen with 4 parts of oxygen. It will not be possible to separate this mixture into its constituents, on account of the equal diffusion of oxygen and hydrogen when thus mixed. The identity of the spectra of helium prevent us from deciding which is the pure gas and which is the mixture. Calculation establishes that if we suppose the heavier gas is a mixture, the density of the lighter, supposed pure, ought to be 1.58. Helium, lastly, if it consists of a mixture of two gases, is formed either of two gases of the densities 2.366 and 1.874, or of two gases of the densities 2.133 and 1.580.

But although this explanation is the most suitable, there exists another which deserves our attention. The spectrum of these two fractions shows no difference. It is not probable that two gases exist the densities of which are so near each other. The different gases do not possess a refraction proportional to their densities. It seems to us that we might admit that we have effected a real separation of the light mols. from the heavy mols. The idea that all the mols. of a gas are homogeneous has never been submitted to the test of experiment. We do not know of any attempt at a separation of this kind of a gas regarded as homogeneous into two different parts. But our experiments show that this question deserves to be studied. If it can yield us similar results we must change our ideas on the nature of matter. — *Comptes Rendus*, vol. cxxiii., p. 214.

A NOTE ON THERMOMETERS.

By Dr. T. L. PHIPSON.

FOR some time past it has been part of my laboratory work to examine thermometers used in the rooms of invalids, as well as some constantly employed for industrial purposes or for meteorological observations.

All physicists are aware how necessary it is to test, now and then, all kinds of thermometers, even those of the best makers, in order to take into account any erroneous indication which may be the result of dilatation or contraction of the glass reservoir. But errors of this kind are, according to my experience, not very common, and rarely reach to 1° C. in a well-made instrument. Nevertheless, it is necessary to know them; and for this purpose all new thermometers used for scientific research should be examined at least once a year, until they are found to be invariable.

Clinical thermometers having a very limited scale, and being, as a rule, most carefully made, do not appear so liable to error as the ordinary laboratory thermometer. Two clinical thermometers, made in London, which have been used by me for the last fifteen years, have not varied one with the other in the slightest manner during the whole of that time.

The ordinary laboratory thermometer is supposed to be thoroughly tested by the makers, and is sometimes guaranteed; nevertheless, the discrepancies noted in boiling-points and melting-points, given by chemists of high standing, appear to indicate that a faulty thermometer is more likely to be the cause of these discrepancies than inexperienced manipulation or impurities in the substance examined.

With regard to thermometers used in the sick room, and in the household generally, I have found very great differences. In such cases cheap instruments, which have not been thoroughly tested, are in frequent use; and the employment of an inexact thermometer in the sick room is not devoid of danger. For instance, a patient 80 years of age, suffering from bronchitis, did not cough or suffer from prostration when the thermometer registered 68° to 70° F., but fell into an alarming state of prostration when it rose to 72° or 73°. Now many thermometers, both mercurial and spirit, which I have examined of recent years, have shown errors of 4° or 5° F., and sometimes

even more, and it is very essential that all such instruments used for taking the temperature of sick rooms or hospital wards should be carefully compared from time to time with a standard instrument of known accuracy, or otherwise tested, so that their amount of error may be exactly known.

The same observation holds good, of course, for thermometers used in registering the temperature of the air. In this case two things are most requisite: 1st, an absolutely correct thermometer; and 2nd, that the observation be invariably made at the same hour. Without these conditions are fulfilled such observations are absolutely worthless. For some time I have been puzzled by the exceedingly high temperatures published in *The Standard* as regards the town of Calais, in the daily list of European localities for which the temperature is given at 9.30 a.m. Calais, in this list, invariably registers much higher than Ostend, Dieppe, or Boulogne, which are all in the same neighbourhood on the map of Europe. There is often a difference of more than 10° F. It would be interesting to enquire into the cause of this, as Calais is said to be near the centre or pivot of an upheaval oscillation described by some geologists. But I fear the discrepancy in question may be due simply to a faulty thermometer in use at that place, or that the temperature is not taken strictly at 9.30 a.m.,—though, in these days of accurate scientific work, it is almost impossible to imagine such a thing.

During the severe and prolonged frost of January and February, 1895, a meteorologist in Surrey recorded the temperature at 9.30 a.m. and 9.30 p.m. every day. He used for this purpose an expensive mercurial thermometer. But when I examined this instrument later, I found that it registered 4° F. too high.

As the thermometer is an instrument daily in use, not only in the chemical laboratory and manufactories, but by the physician, the meteorologist, the brewer, the sanitary engineer, and in a host of industries, and as the indications of a faulty instrument (unless the error is known) are not merely worthless, but often costly and dangerous, it may be advantageous to bear in mind the subject of this short note.

The Casa Mia Laboratory, Putney.

ESTIMATION OF SULPHUR IN CAST-IRON OR STEEL.

By G. G. BOUCHER.

FIVE grms. of iron or steel are dissolved in a strong solution of copper ammonium chloride, and when the precipitated copper is dissolved the solution is filtered. The filter-paper and contents are then thoroughly washed with hot distilled water till the washings are free from copper. The sulphur remains on the paper with the graphite and a small quantity of silica and iron. The paper and contents are now placed in a small beaker, and about 30 c.c. of nitro-hydrochloric acid are added; the solution is then boiled and filtered; the filtrate is neutralised with ammonium hydrate, and then made slightly acid with dilute hydrochloric acid. To the solution 5 grms. of barium chloride are now added; the solution is heated, and the barium sulphate allowed to settle. It is then filtered off, well washed, burnt, and weighed.

Instead of dissolving the sulphur out of the residue of graphite, &c., with nitro-hydrochloric acid, the paper and contents may be boiled with bromine-water and a few drops of hydrochloric acid. When the excess of bromine has been boiled off the solution is filtered, and barium chloride added to the filtrate. The solution is heated, &c., as before.

Below I give a few analyses by this process:—

	Nitro-hydrochloric acid method.	Copper-ammonium chloride method.
	Sulphur p. c.	Sulphur p. c.
1. Bessemer iron ..	0'035	0'041
2. " ..	0'012	0'021
3. " ..	0'022	0'024
4. " ..	0'023	0'023
5. " ..	—	1st anal. 2nd anal.
6. Mottled iron ..	0'185	0'020 0'021
		0'192 0'192

This process is particularly adapted for the estimation of small quantities of sulphur, the absence of a large quantity of ferric chloride, and free hydrochloric acid in which barium sulphate is soluble to an appreciable extent, rendering the process extremely accurate.

The percentage of sulphur obtained by this process is higher than that given by any other processes I know of, and the barium sulphate is always white, showing the absence of iron.

The Laboratory, North Lonsdale Iron Works,
Ulverston, August 3, 1896.

ON THE CONTENTS OF PHOSPHORUS AND SULPHUR IN CRUCIBLE STEELS.

By SERGIUS KERN, M.E., St. Petersburg.

I THINK the following table, drawn out by me after many years of work with crucible steels, the manufacture of which has been my special care, may be of some use to metallurgists.

Formula for the Contents of Phosphorus + Sulphur in Crucible Steels.

	P+S. Joint per cent.
Tool Steel—	
Best	0'03
Fair	0'04
Middling (rather suspicious)	0'05
Projectiles	0'03

In this sum it is preferable to have the sulphur as low as possible, say, 0'19 per cent (maximum). This was the strong conviction of my good friend of my good friend the late M. Antoine Rollet.

	P+S. Joint per cent.
Steel Castings—	
Best	0'05
Fair	0'08
Suspicious	0'10

All castings to be imperatively annealed.

JAPANESE COAL.

By FRANK BROWNE, F.C.S.,
Acting Government Analyst, Hongkong.

THE sample examined was that variety known as Tubari coal, from the island of Yezo. It was in large black lumps, which when broken up gave a dark chocolate-brown powder. It burned readily, giving at first a bright smoky flame, which disappeared after a short time, leaving a glowing mass. It is a non-caking coal. The results of the analysis show high percentages of volatile combustible matter and of ash.

It consisted of—

Moisture	3'83
Volatile combustible matter ..	36'62
Fixed carbon	42'70
Ash	16'85

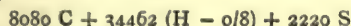
100'00

Ultimate analysis of the dried coal gave—

Carbon	62.84
Hydrogen	6.37
Nitrogen	1.08
Oxygen (calculated)	11.01
Sulphur (combustible)	1.18
Ash (containing 0.49 per cent of sulphur)	17.52
	100.00

The relative density (water at 15.5° = 1) was 1.411.

The heat of combustion calculated from the following formula—



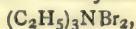
gave 6826 calories.

ON THE
EXISTENCE OF PENTAETHYL NITROGEN.*

By ARTHUR LACHMAN.

THERE is *a priori* no reason why nitrogen in its pentavalent state cannot combine with five like atoms or radicals, just as in its trivalent state it unites with three like atoms. And there is, further, no reason known why in pentavalent nitrogen compounds the atoms or radicals attached to the nitrogen must consist of two groups, strongly contrasted (e. g., $\text{H}_4 \equiv \text{N}-\text{Cl}$, $(\text{CH}_3)_3 \equiv \text{N} = \text{ICl}$, $\text{C}_6\text{H}_5-\text{N} \equiv \text{O}_2$). The existence of a compound NX_5 , therefore, is not contradicted by anything but experience, and it seemed well worth the effort to attempt its preparation. The pentachloride, NCl_5 , was not to be thought of; the hydrogen compound, NH_5 , presented no point of attack; but for the pentaethyl compound, $\text{N}(\text{C}_2\text{H}_5)_5$, one method in particular suggested itself, which has been very frequently employed in the carbon series, and which had been successful in the one case where it was tried with (trivalent) nitrogen.

This method is the action of zinc alkyl on alkyl halogen substitution products of the hypothetical compound, NH_5 . Tertiary butyl iodide (*Ann. Chem.*, Liebig, clxv., 107), $(\text{CH}_3)_3\text{CI}$, reacts immediately with zinc ethyl, and tetraethylammonium iodide, $(\text{C}_2\text{H}_5)_4\text{NI}$, seems to be structurally analogous. Triethylamine dibromide,†



appears to present even a more favourable case, as Tscherniak (*Ber. d. Chem. Ges.*, ix., 143) had successfully prepared triethylamine by the action of zinc ethyl on ethyldichloramine, $(\text{C}_2\text{H}_5)_2\text{NCl}_2$. The experiments were confined to these two substances.

Action of Zinc Ethyl on Tetraethylammonium Iodide.

Strange to say, tetraethylammonium iodide and zinc ethyl do apparently react. The action is very slow; heating on the water-bath for several hours produces no effect, nor does standing at ordinary temperature for ten days. But if, after standing from four to six weeks, a mixture of the substances in question (slightly diluted with ether to give fluidity to the mass) is poured into water and filtered from the zinc hydrate‡, the solution possesses a strongly alkaline reaction. It slowly turns yellow, and then a finely crystalline red precipitate sepa-

rates. This precipitation is not hastened by carbon dioxide; in the experiment that was carefully controlled it required a day and a half for completion.

Ten grms. tetraethylammonium iodide, 5 grms. zinc ethyl, and 15 c.c. ether, stood for forty-three days at the ordinary working temperature, and yielded 0.61 grm. of the red substance. This red substance, by properties and analysis, seems to be tetraethyl ammonium triiodide, $(\text{C}_2\text{H}_5)_4\text{NI}_3$. (Found 73.4 per cent iodine, calculated 74.5 per cent; the crude product was analysed directly).

I am at a loss to explain this curious reaction. The formation of an alkaline* substance is in itself peculiar. The alkaline body could not be isolated nor in any way identified, owing to the very small quantity formed; in evaporating the solution saturated with carbon dioxide, the alkaline reaction disappeared. The precipitation of tetraethylammonium triiodide from an alkaline solution, which could not have contained any free iodine, is quite inexplicable.

Action of Zinc Ethyl on Triethylamine Dibromide.†

This reaction presented three possibilities:—

- I. $(\text{C}_2\text{H}_5)_3\text{NBr}_2 + \text{Zn}(\text{C}_2\text{H}_5)_2 = (\text{C}_2\text{H}_5)_5\text{N} + \text{ZnBr}_2$.
- II. $(\text{C}_2\text{H}_5)_3\text{NBr}_2 + \text{Zn}(\text{C}_2\text{H}_5)_2 = (\text{C}_2\text{H}_5)_4\text{NBr} + \text{Zn}(\text{C}_2\text{H}_5)\text{Br}$.
- III. $(\text{C}_2\text{H}_5)_3\text{NBr}_2 + \text{Zn}(\text{C}_2\text{H}_5)_2 = (\text{C}_2\text{H}_5)_3\text{N} + \text{C}_2\text{H}_5\text{Br} + \text{Zn}(\text{C}_2\text{H}_5)\text{Br}$.

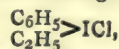
Reactions I. and II. would represent actual syntheses; reaction III. would involve reduction. Experiment showed that reaction III. took place to the exclusion‡ of the others. It seems superfluous to give the details of work which has no preparative value; but every product of the action was identified. As a matter of fact, in some cases where the mixture of zinc ethyl and the dibromide (always diluted with considerable chloroform) was allowed to stand several hours, as much as 33 per cent of the total nitrogen employed was obtained as tetraethylammonium bromide; but this was due to a secondary action,—the addition of ethyl bromide to triethylamine,—for, if the mixture was examined shortly after its preparation, no quaternary ammonium compound could be found.

No synthesis whatever, then, had been accomplished. Triethylamine dibromide, in its action toward zinc ethyl, behaves merely as a mixture of triethylamine and bromine. It will be interesting to learn from Dr. Norris whether it behaves thus in every case. In this connection it may be remarked that ethyl dichloramine, which reacts normally with zinc ethyl, acts like free chlorine in some instances (*Ber. d. Chem. Ges.*, xvi., 1047).

Perhaps pentaethyl nitrogen will be prepared by some one more fortunate, by means at present undiscernible. The experiments just sketched will not be continued.

Action of Zinc Ethyl on Phenyl Iodide Chloride.

This may be the place to briefly give an account of the action of zinc ethyl on phenyl iodide chloride, $\text{C}_6\text{H}_5\text{I}.\text{Cl}_2$, which possesses some analogy to triethylamine dibromide, and the study of which I took up for that reason. Both are halogen addition-products, a sort of half-way station between the more stable derivative of elements exhibiting two valencies. One might reasonably expect to obtain, in this case, a semi-aliphatic analogue,—



of the very stable iodonium compounds of Hartmann and Viktor Meyer. The reaction, however, is exactly analogous to that of the dibromide: phenyl iodide, ethyl chloride,

* Contribution from the Laboratory of General Chemistry of the University of Michigan. From the *American Chemical Journal*, vol. xviii., No. 5, May, 1896.

† The kindness of Dr. J. F. Norris enabled me to use this compound instead of the more difficultly accessible $(\text{CH}_3)_3\text{NCl}$.

‡ It was impossible to determine satisfactorily whether this zinc hydrate contained basic zinc iodide, and thus ascertain whether the zinc ethyl had reacted in the usual manner. The hydrate retained tetraethylammonium iodide so tenaciously that even after washing for several days with water and alcohol the filtrate still gave a distinct reaction with silver nitrate.

* It is not impossible that this alkaline substance is really pentaethyl nitrogen, but alkalinity is hardly a property it would be expected to possess.

† This was prepared according to Remsen and Norris. *American Chemical Journal*, xviii., 90.

‡ A minor reaction, represented by the equation —
 $(\text{C}_2\text{H}_5)_3\text{NBr}_2 + \text{Zn}(\text{C}_2\text{H}_5)_2 = (\text{C}_2\text{H}_5)_5\text{N} + \text{C}_2\text{H}_5\text{Br} + \text{ZnBr}_2$, also took place.

zinc chloride, and zinc oxychloride are the final products. There are indications that an unstable intermediate addition-product is formed. It was possible to show analytically that almost exactly half of the total chlorine was regained as zinc chloride (and oxychloride); the other half could not be accurately traced: the phenyl iodide was recovered unaltered, and in practically theoretical quantity, but only a small percentage of ethyl chloride could be isolated.

THE PREPARATION OF ALLYLENE, AND THE ACTION OF MAGNESIUM UPON ORGANIC COMPOUNDS.

By EDWARD H. KEISER.

As described in a previous paper (*Journal of the Franklin Institute*, Jan., 1895) metallic magnesium at a low red heat acts energetically upon the vapours of the alcohols. The metal glows and is converted into a black coherent mass. This black residue, when put into water, evolves a gas which consists chiefly of hydrogen and allylene. The evolution of gas becomes very rapid if a few drops of ammonium chloride solution are added to the water. The hydrogen and allylene can be readily separated from one another by conducting the mixed gases through a series of wash-bottles containing an ammoniacal solution of silver nitrate; the allylene is thereby converted into the insoluble silver allylide, AgC_3H_3 , while the hydrogen passes through unchanged.

The best yield of allylene in the earlier experiments was obtained from the magnesium that had been heated in the vapours of propyl or of allyl alcohols. Recent experiments have shown that a more advantageous method of preparing the hydrocarbon is to heat magnesium powder in the vapour of acetone, and to decompose the black mass thus obtained with water. In the method of preparation now adopted a layer of magnesium powder is put into a thin-walled iron tube, which is as long as the combustion-furnace that is to be subsequently employed for heating it. The iron tube is closed with asbestos stoppers, and through these stoppers glass tubes are passed; so that the acetone vapour may be conducted in at one end of the iron tube, and the gases formed during the reaction may be drawn off at the other end. The acetone is converted into vapour by boiling the liquid in a flask which is connected with one end of the iron tube containing the magnesium. After the air is driven out of the apparatus the iron tube is heated in the combustion-furnace. At a low red heat the action begins; the magnesium becomes red-hot, and finally the glowing extends throughout the entire mass of the metal. When this has taken place the contents of the tube are allowed to cool down in the acetone vapour; the black mass is then removed from the tube, and, since the moisture of the air acts upon it, it is best to preserve it in a tightly stoppered bottle. To obtain allylene from this residue it is only necessary to put it into a flask containing water to which a few drops of ammonium chloride solution have been added. The gas given off consists mainly of allylene and hydrogen, the latter gas being obtained from the magnesium that has remained unacted upon.

In order to throw light upon the nature of the reaction that takes place when magnesium acts upon the alcohols and upon acetone, the gases that escaped from the tube while the magnesium was glowing were collected in gasometers over water. These gases were analysed, and the results of the analyses are given in the following table. (See next column).

From the very small quantities of oxides of carbon in these gases it seems probable that the magnesium combines with the oxygen of the alcohols; hydrogen and hydrocarbons are thereby formed, and at the elevated

Alcohols.	CO_2 .	CO .	Unsaturated hydrocarbons.	Saturated hydrocarbons.	Hydrogen.
Methyl ..	0.8	0.6	—	19.7	78.9
Ethyl ..	—	0.4	14.0	11.1	74.5
Propyl ..	—	3.5	17.8	19.9	58.8
Isopropyl ..	—	0.2	12.2	15.4	72.2
Isobutyl ..	—	0.5	11.4	14.4	73.7
Amyl ..	1.0	—	20.4	22.3	56.3
Tertiary amyl (a)	—	—	24.3	17.5	58.2
„ (b)	0.2	—	22.4	17.9	59.3
Secondary octyl (a)	—	0.5	26.0	24.5	49.0
„ (b)	0.6	1.6	25.2	25.8	46.8

temperature of the reaction a portion of the magnesium unites with the carbon and hydrogen of these compounds, forming magnesium allylide. The black residue contains, besides the magnesium oxide and magnesium allylide, a quantity of free carbon. Attempts have been made to extract the allylide by means of solvents, but thus far it has not been possible to obtain a solvent for it. That magnesium allylide is present in the black mass is shown not only by the action of water upon it, whereby allylene is evolved which has been transformed into the silver, the mercury, and the copper compounds which characterise this hydrocarbon; but also by the fact that it contains from 0.3 to 0.4 per cent of hydrogen, as has been found by burning weighed quantities of it in a stream of oxygen. Further experiments have shown that when the magnesium is heated in an atmosphere containing no hydrogen, as, for instance, in carbon monoxide or carbon dioxide, and the residue thus obtained is decomposed by water, the gas evolved gives scarcely any precipitate with ammoniacal silver solution, the small traces of silver allylide thus obtained being formed from the hydrogen which is occluded in the metallic magnesium.

The black mass, consisting of magnesium oxide, carbon, and magnesium allylide obtained by the glowing of magnesium in the vapours of acetone and of the alcohols, was in each case treated with water, and the gases evolved were conducted through an ammoniacal solution of silver nitrate. The silver precipitates were removed by filtration, and, after washing and drying, were analysed. The following table contains the results of the analyses:—

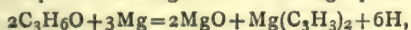
Magnesium allylide from	Analyses of silver precipitates.		
	Wt. taken.	Wt. AgCl found.	Per cent Ag.
Acetone	0.1617	0.1577	73.40
Methyl alcohol	0.1292	0.1270	73.97
Ethyl „ { (a)	0.1163	0.11365	73.53
„ { (b)	0.0979	0.09615	73.89
Propyl „	0.15605	0.1522	73.39
Isopropyl „ { (a)	0.27308	0.26802	73.58
„ { (b)	0.10244	0.10114	74.31
Allyl „ { (a)	0.16705	0.1620	72.97
„ { (b)	0.17185	0.16735	73.27
Isobutyl „	0.1301	0.1289	74.56
Amyl „ { (a)	0.18156	0.17933	74.34
„ { (b)	0.1365	0.13767	75.90
Tertiary amyl „	0.08509	0.08374	74.07
Calculated for AgC_3H_3	..	..	73.45

The comparatively close agreement of these results with the theoretical value for silver in silver allylide indicates that the silver precipitates were most probably pure compounds. The copper allylide was made by conducting the gases from the evolution flask through an ammoniacal solution of cuprous chloride. The greenish yellow precipitate was filtered and washed thoroughly with water, and, after drying in desiccators, was analysed.

Found 62.1 and 62.2 per cent of Cu.
Calculated for CuC_3H_3 , 61.98 per cent.

The mercury allylide has also been prepared. When first formed it is a white flocculent precipitate. It was purified by dissolving it in boiling alcohol. On cooling it crystallised out in the form of slender needles. These crystals possessed the properties of the mercuric allylide described by Kutscheroff (*Ber. d. Chem. Ges.*, xvii., 26).

Experiments have also been made to determine the yield of allylene obtained by this method of preparation. If it be assumed that the magnesium acts upon the acetone vapour according to the following equation—



then the residual magnesium mass should contain 3.3 per cent of hydrogen. Determinations of hydrogen by combustion gave on an average 0.37 per cent; so that the yield would be about 0.1 of the theoretical amount. Further, 10 grms. of the magnesium residue gave about 0.7 grm. silver precipitate.

Further experiments with the allylene are in progress. The gas is readily absorbed by concentrated sulphuric acid. It is probable that a sulphonc acid is thus formed. The sulphuric acid, after having absorbed a large volume of the gas, was diluted with water and neutralised with barium carbonate. After filtration the clear solution on evaporation gave a deposit of a crystalline barium salt. The composition of this compound is now being determined.

In conclusion, I desire to express my thanks to Miss Mary B. Breed and Miss Lucy Francisco for their careful work in making the analyses and in assisting me in the experiments described in this paper. — *American Chemical Journal*, vol. xviii., No. 4.

THE ACTION OF LIGHT ON SOME ORGANIC ACIDS IN THE PRESENCE OF URANIUM SALTS.*

By HENRY FAY.
(Concluded from p. 70).

Decomposition of Acetic Acid.

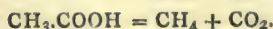
VARIOUS attempts were made to decompose acetic acid in the same manner as propionic and isobutyric acid, but it was decomposed only with difficulty. The only proportions which were found to give off gas was when 15 c.c. glacial acetic acid and 5 c.c. strong solution of uranyl acetate were exposed. From this solution gas was given off, but only extremely slowly. The exposure was made in April and May, about six weeks being required to give enough for analysis. The clear yellow solution did not to any extent change to the green, so characteristic in all the other cases. There was a slight green colour, but it was not marked.

Analysis of gas:—

13.4 c.c. of gas gave 6.4 c.c. CO₂.

Volume of original gas 13.2 m.m. = 1 vol.
Volume after addition of oxygen 108.24 " = 8.2 vols.
Volume after explosion 80.52 " = 6.1 "
Contraction = 2.1 "

Calculated contraction for CH₄ is 2 volumes, while that found is 2.1 volumes, which shows the gas to be methane, and the decomposition is to be represented by the equation—



It is interesting to note that the power of decomposition ceases with acetic acid, which breaks down under

the influence of light only with difficulty. The power is apparently lost in formic acid, and it has been impossible so far to effect any decomposition of this acid by light in the presence of uranium salts.

Comparison of the Rates of Decomposition of Propionic, Butyric, and Isobutyric Acids.

For the purpose of comparing the relative rates of decomposition of these three acids, tenth-normal solutions of each were made, and varying quantities of the acid were exposed with varying quantities of uranyl nitrate. It was decided to use propionic acid as the standard in determining the best conditions possible. The following table shows the comparison between two solutions of propionic acid exposed under exactly similar conditions:—

No. of days.	Hours of exposure.	Amount of gas collected. No. 1.	No. 2.	Condition of weather.
1	2	0.8	0.6	Clear.
2	7½	2.8	2.8	"
3	7½	3.4	4.8	"
4	7½	4.0	7.2	"
5	15	4.3	9.2	"

Solution No. 1 contained 10 c.c. one-tenth normal nitrate, UO₂(NO₃)₂.6H₂O, and 10 c.c. one-tenth normal propionic acid.

Solution No. 2 contained 15 c.c. one-tenth normal propionic acid and 5 c.c. one-tenth normal nitrate, UO₂(NO₃)₂.6H₂O.

It will be seen that the solution containing the larger amount of acid acted the more rapidly. The comparison is not exactly fair, as the precipitate, which is formed some time after the decomposition begins, has some effect, as will be seen in the following table, in which is given a comparison of propionic, butyric, and isobutyric acids. Each solution contains 15 c.c. one-tenth normal acid and 5 c.c. one-tenth normal nitrate, UO₂(NO₃)₂.6H₂O.

No. of days.	Propionic.	Amount of gas collected, Isobutyric.	Butyric.
1	1.2	1.4	1.0
2	2.5	3.0	2.5
3	4.0	4.7	3.6
4	5.3	5.7	4.3
5	5.3	5.7	4.3
6	6.5	6.4	4.9
10	7.6	7.4	5.8
11	8.8	8.4	—
12	10.2	9.5	—
13	12.0	10.6	9.0
14	13.6	11.4	9.6
15	15.0	12.4	10.5
16	15.8	12.8	11.2
17	16.3	13.0	11.2

It will be seen that on the sixth day the amount of gas collected from the propionic acid and the isobutyric acid is practically the same. Up to this time there was only slight cloudiness in the solutions, but after three days of rain a precipitate was found in the solution containing isobutyric acid. From this time on it will be seen that there is a gradual gain in the amount of gas collected from the propionic acid over the amount collected from the isobutyric acid.

As the weather was unfavourable for carrying these comparisons any further, the subject was dropped at this point, but it is believed that interesting comparisons can be obtained by working during the summer months.

Summary.

It has been shown that the precipitate in the solution of uranyl oxalate and oxalic acid is formed in two stages: (1) formation of uranous oxalate, (2) formation of the purplish brown precipitate from the uranyl oxalate left in solution. The nature of the latter has not been cleared

* From the author's Thesis, submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy, June, 1895. The work was undertaken at the suggestion of Professor Remsen and carried on under his supervision. From the *American Chemical Journal*, xviii., No. 4.

up, but it is shown to contain carbon, and consequently cannot be the hydrated oxide as supposed. The formic acid found when oxalic acid is decomposed must come from the oxalic acid itself, as all attempts to build it up from water and carbon monoxide in presence of uranium salts have failed.

Tartaric acid, when exposed with uranium salts to the sunlight, forms an insoluble precipitate with uranium, the nature of which has not been cleared up.

It has finally been shown that acetic, propionic, and isobutyric acids decompose into the hydrocarbons corresponding to the acids and into carbon dioxide.

OXIDATION OF SODIUM SULPHIDE AND HYDROSULPHIDE TO THE SULPHATE BY ELECTROLYSIS.*

By FRANK W. DURKEE.

(Concluded from p. 71).

DRAWING air through solutions of sodium sulphide, according to Lunge ("Soda Industry," p. 531), first produces sodium hydroxide and sodium thiosulphate, $2\text{Na}_2\text{S} + 4\text{O} + \text{H}_2\text{O} = 2\text{NaOH} + \text{Na}_2\text{S}_2\text{O}_3$. The thiosulphate then takes oxygen from the air and forms sodium sulphate, and sulphur separates, $\text{Na}_2\text{S}_2\text{O}_3 + \text{O} = \text{Na}_2\text{SO}_4 + \text{S}$. Afterwards yellow polysulphides result from the solution of the free sulphur in sodium sulphide and hydroxide, come in contact with more oxygen, sulphur separates again, and an additional amount of thiosulphate is produced, $\text{Na}_2\text{S}_5 + 3\text{O} = \text{Na}_2\text{S}_2\text{O}_3 + 3\text{S}$ (Dopping, *Ann. Chem.* (Liebig), xlvii., 172). Very likely other polysulphides are produced, but are all changed to the thiosulphate by the free oxygen, according to similar reactions.

If, therefore, the electrolytic oxidation of sodium sulphide to the sulphate takes place as above described, at any instance after the electric current has acted on the solution for some time, and, indeed, until very near the end of the electrolytic oxidation, the sum of the weights of sodium in the sulphide, hydroxide, sulphate, thiosulphate, and polysulphide, must equal the weight of sodium in the solution of sodium sulphide before electrolysis. Moreover, if these weights do equal each other, it follows that the oxidation takes place through the formation of these compounds and no others. So, to settle the point under consideration, it is only necessary to subject solutions of sodium sulphide to electrolytic action for different periods of time, and then to rigorous quantitative analysis, in order to determine whether the oxidation takes place according to the above reactions or not.

For convenience, the sulphide solutions, intended for analysis and described below, have been numbered.

Number I. was prepared by supersaturating with hydrogen sulphide 50 c.c. of the solution of sodium hydroxide, already described and analysed, and adding 50 c.c. more of the same solution of sodium hydroxide. After diluting with 300 c.c. of water, the solution was subjected to electrolysis, in the apparatus before used. A 3.1 ampère current passed for one hour and thirty minutes, after which the solution was filtered and made up to 1000 c.c. by addition of water. Numbers II., III., IV., and V. were prepared by the method used in the preparation of No. I., but the electric current and time of electrolysis varied in each case. No. II. was subjected to the action of a 3.1 ampère current for two hours; No. III. to a 3.2 ampère current for two hours and thirty minutes; No. IV. to a 3.0 ampère current for two hours and thirty minutes; No. V. to a 3.1 ampère current for six hours and forty minutes. As a high-reading ampère metre was used a part of the time, in some cases, the above figures representing ampères may not be entirely reliable.

* *American Chemical Journal*, July, 1896.

In 50 c.c. of the electrolytes, which, theoretically contain as much sodium as 5 c.c. of the solution of sodium hydroxide, the determination of sodium in the different compounds has been made by the following analytical methods:—To get the weight of sodium in the sulphate, hydrochloric acid and barium chloride have been added to 50 c.c. of the electrolytes, and the resulting barium sulphate determined in the usual way. The weight of sodium in sodium sulphate has then been calculated from the weight of barium sulphate obtained.

The weight of sodium in sulphides has been obtained by use of standard zinc solution, prepared by dissolving 3.253 grms. of pure zinc in hydrochloric acid and adding ammonia to supersaturate the liquid. Enough water was then added to make 1000 c.c. Nickel nitrate upon a white plate has been used as indicator in these titrations.

The first step in the method used for the determination of sodium in the form of the thiosulphate has been to add to the solution a slight excess of the zinc solution described above. The resulting sulphide of zinc and free sulphur have then been filtered off, excluding the air as much as possible meanwhile, and excess of bromine has been added to the filtrate to oxidise the thiosulphate to acid sulphate. After acidifying with hydrochloric acid, an excess of barium chloride has been added, the weight of the barium sulphate afterward determined in the usual way, and from it the corresponding weight of sodium calculated. By subtracting from this the weight of sodium found in sodium sulphate, twice the weight of the sodium combined in the thiosulphate has been obtained.

In the determination of sodium in the form of hydroxide, a large excess of standard sulphuric acid has been added to 50 c.c. of the electrolyte solutions. Afterwards they have been rapidly boiled to expel sulphur dioxide and hydrogen sulphide, filtered, and titrated back with standard sodium hydroxide, using methyl-orange in cold solution as indicator. By subtracting the weight of the sodium in the standard solution of sodium hydroxide used, from the weight of sodium that the standard sulphuric acid would neutralise, the weight of sodium acted upon by the standard sulphuric acid in the electrolyte solution under examination has been obtained. The difference between this weight of sodium and the sum of the weights of sodium in sulphides and thiosulphate equals the weight of sodium in the hydroxide.

For the sake of comparison, the analytical results have been arranged in tabular form. The results themselves are averages obtained in duplicate determinations. The weights are given in grms.:

Solutions.	No. I.	No. II.	No. III.	No. IV.	No. V.
Time	1 h.	2 h.	2 h.	3 h.	6 h.
	30 m.	2 h.	30 m.	30 m.	40 m.
Ampères	3.1	3.1	3.2	3	3.1
Ampère-hours ..	4.6	6.2	8	10.5	20.7
Na in Na_2SO_4 ..	0.0251	0.0441	0.0563	0.0915	0.1604
Na in Na_2S ..	0.1096	0.0806	0.0515	0.0354	—
Na in $\text{Na}_2\text{S}_2\text{O}_3$..	0.0131	0.0158	0.0145	0.0086	0.0019
Na in NaOH ..	0.0236	0.0320	0.0492	0.0367	0.0090
	0.1714	0.1725	0.1715	0.1722	0.1713

Barring experimental errors in the preparation of the standard solution subjected to electrolysis and analysis, each should contain 0.1718 grm. of sodium per 50 c.c. It will be seen that the weight of sodium in sodium thiosulphate plus sodium in the hydroxide, sulphate, and sulphides corresponds so closely to the theoretical weight of sodium in 50 c.c. of the solution that it seems impossible to have the oxidation take place through the formation of any compound or compounds of sodium besides those above mentioned. Sulphides disappear first, the hydroxide next, and the thiosulphate last of all.

The method used for the estimation of the polysulphides of sodium is based upon the fact that, when an alkaline solution of zinc chloride is added to a solution of poly-

sulphides, the sulphur above one atom separates out, and zinc sulphide is produced. The free and combined sulphur can then be filtered off, oxidised to sulphuric acid and zinc sulphate by bromine, and calculated from the weight of the barium sulphate which results on addition of hydrochloric acid and barium chloride. The resulting weight of sulphur is that of all the sulphur in sulphides and polysulphides. By subtracting the weight of sulphur that would combine with the weight of sodium, found by means of the standard solution of zinc chloride, to form sodium sulphide, the weight of sulphur in the polysulphides of sodium above one atom has been obtained.

Solutions I., II., III., and IV. gave the following weights (in grms.) of sulphur above one atom in the polysulphides:—

I.	II.	III.	IV.
0.0208	0.0256	0.0415	0.0199

These determinations are valuable inasmuch as they show the amount of polysulphide present at different stages of the electrolysis, and correspond, as nearly as could be judged, to the varying intensity of the yellow colour in the solutions.

The effect of a 3-ampère current at 50 volts, alternating 130 times per second, was next tried upon three sulphide solutions.

Platinum wire, either double or single, was used for the electrodes. After the electrolysis, the solutions were filtered and diluted with water to 1000 c.c. Theoretically, therefore, 50 c.c. of No. I. contain 0.1716 gm. of sodium; No. II., 0.1802 gm.; and No. III., 0.1802 gm. The methods used in the analyses of the solutions obtained by use of the direct current and already described have been used over again in the analysis of I., II., and III., and the results are below. The weights are given in grms.

Solutions.	No. I.	No. II.	No. III.
Approximate time of electrolysis	2 h.	3 h.	30 m.
Approximate number of ampères	3	3	3
Na in Na ₂ SO ₄	0.0033	0.0107	0.0218
Na in Na ₂ S	0.1596	0.1152	0.0857
Na in Na ₂ S ₂ O ₃	0.0022	0.0249	0.0368
Na in NaOH	0.0058	0.0299	0.0361
	0.1709	0.1807	0.1804

It would appear from these results, therefore, that the oxidation of sodium sulphide to sulphate by means of the alternating current is the same, so far as chemical changes are concerned, as oxidation by the direct current. The rate of oxidation, using platinum wire electrodes, is, of course, much slower with the alternating current than with the direct when large electrodes were used. However, if the electrolysis were continued long enough, there is no reason to suppose that all the sulphide in the electrolyte could not be oxidised to sulphate. In these experiments it was not considered advisable to carry an electrolysis beyond five hours, inasmuch as the platinum electrodes dissolved under the combined influence of the alternating current and electrolyte, which never happened when the direct current was employed. Some idea of the rapidity with which platinum dissolves under the above conditions can be obtained from a platinum determination made in Solution II.; 100 c.c. gave 0.0216 gm. platinum. At the end of the electrolysis, therefore, the platinum electrodes weighed 0.216 gm. less than at the beginning. Judging from the red colour in the electrolytes and the precipitation of platinum sulphide when acids were added, sodium thioplatinate was produced. This part of the subject, however, needs further investigation.

Pure Ether for Narcotising.—H. Thoms (*Berichte der Pharm. Gesell.*).—Ether, most carefully purified, is not neutral to litmus-paper, but gives a bluish tint to sensitive red litmus-paper.

THE INTRODUCTION OF STANDARD METHODS OF ANALYSIS.*

By the Baron HANNS JÜPTNER VON JONSTORFF
(Neuberg, Austria).

IN compliance with an invitation from the Council of the Iron and Steel Institute, I have pleasure in presenting the following account of the introduction of standard methods in the analysis of iron and steel.

In the first place I must point out that the phrase "introduction of standard methods of analysis" is, strictly speaking, a catch word, and that it would perhaps have been better to speak of a unification of analytical results. Adopting the most general standpoint, it may be said that the only important point to be attained is to ensure that analyses of one and the same sample made by different individuals shall agree well together, and give as accurate results as possible; and further, that it can be considered somewhat a matter of indifference whether this object is attained by the use of similar methods or in any other possible way. Indeed, it will be seen subsequently that considerable objections may be raised against the introduction of standard methods for general use.

That this object is not at the present time attained in many cases is generally known. Nevertheless I shall venture to cite some examples of analytical differences which may not be without interest, inasmuch as the analyses in question were made, not by beginners, but by experienced, and even eminent, analysts.

A chill-roll (Jüptner, *Fortschritte im Eisenhüttenlaboratorium*, 1895, vol. i., p. 3) was examined in two laboratories (A and B), and as quite incredible differences were obtained, a check analysis (C) was made. The results were as follows:—

	A.	B.	C.
	Per cent.	Per cent.	Per cent.
Carbon	3.50	2.785	2.767
Silicon	1.30	0.668	0.677
Manganese	2.40	trace	0.050

In one and the same steel sample two laboratories found:—

	A.	B.
	Per cent.	Per cent.
Phosphorus	0.11	0.0870
Arsenic	no trace	0.0387
Total	0.11	0.1257

In one and the same laboratory there was found in the same sample of pig iron which was sent for analysis twice under different designations:—

	Per cent.	Per cent.
Combined carbon	0.91	0.617
Graphite	2.67	3.033
Total carbon	3.58	3.650
Silicon	2.65	1.179
Manganese	0.088	0.105
Phosphorus	0.355	0.394

Happily, however, such enormous differences are rarely met with; but the fact that they can occur at all is undoubtedly a matter for reflection, and renders it a pressing duty to devise a method of obviating such occurrences.

Notwithstanding most careful and frequent repetitions of the analyses, differences are still met with which under some circumstances may be considerable. Thus the investigation of four standard samples by the English, Swedish, and American Committees gave, according to J. W. Langley (*Journal of the American Chemical Society*, 1893, p. 448) the following results:—

* Read before the Iron and Steel Institute.

Stand- ard.	Constituents.	English Commisn.	Swedish Commisn.	American Commisn.	Max. Diff.
I.	Carbon ..	0.414	0.450	0.440	0.036
	Silicon ..	0.203	0.257	0.270	0.013
	Sulphur ..	0.006	0.008	0.004	0.004
	Phosphorus ..	0.018	0.022	0.016	0.006
II.	Manganese ..	0.259	0.282	0.254	0.028
	Carbon ..	0.816	0.840	0.807	0.033
	Silicon ..	0.191	0.185	0.207	0.017
	Sulphur ..	0.007	0.004	0.004	0.003
III.	Phosphorus ..	0.014	0.015	0.010	0.005
	Manganese ..	0.141	0.145	0.124	0.021
	Carbon ..	0.476	0.500	0.452	0.048
	Silicon ..	0.141	0.150	0.152	0.011
IV.	Sulphur ..	0.008	0.006	0.004	0.004
	Phosphorus ..	0.021	0.021	0.015	0.006
	Manganese ..	0.145	0.170	0.140	0.030
	Carbon ..	0.151	0.170	0.160	0.019
V.	Silicon ..	0.008	0.015	0.015	0.007
	Sulphur ..	0.039	0.048	0.038	0.010
	Phosphorus ..	0.078	0.102	0.088	0.024
	Manganese ..	0.130	0.130	0.098	0.032

The examination of the four samples by the chemists of the British Committee gave the following results:—

Stand- ard.	Constituents.	W. Jen- kins.	G. S. Packer.	J. Pat- tinson.	E. Riley.	J. E. Stead.	Max. Diff.
I.	Carbon ..	0.43	0.44	0.393	0.387	0.419	0.053
	Silicon ..	0.260	0.28	0.271	0.250	0.252	0.030
	Sulphur ..	0.010	traces	trace	0.004	0.007	0.010
	Phosphorus ..	0.02	0.017	0.019	0.017	0.016	0.004
II.	Manganese ..	0.26	0.267	0.263	0.278	0.229	0.049
	Carbon ..	0.82	0.85	0.802	0.811	0.796	0.054
	Silicon ..	0.200	0.197	0.182	0.192	0.186	0.018
	Sulphur ..	0.008	traces	0.007	0.007	0.007	0.008
III.	Phosphorus ..	0.02	0.012	0.012	0.012	0.012	0.008
	Manganese ..	0.14	0.144	0.145	0.140	0.137	0.008
	Carbon ..	0.55	0.46	0.461	0.456	0.455	0.095
	Silicon ..	0.144	0.14	0.140	0.153	0.130	0.023
IV.	Sulphur ..	0.015	traces	trace	traces	0.008	0.015
	Phosphorus ..	0.02	0.022	0.022	0.016	0.024	0.008
	Manganese ..	0.13	0.130	0.158	0.144	0.161	0.031
	Carbon ..	0.165	0.146	0.142	0.147	0.154	0.013
V.	Silicon ..	0.008	0.008	0.009	0.008	0.009	0.001
	Sulphur ..	0.040	0.036	0.040	0.041	0.040	0.005
	Phosphorus ..	0.08	0.08	0.075	0.081	0.075	0.006
	Manganese ..	0.13	0.130	0.130	0.124	0.137	0.013

The examination of the fifth standard sample by the English Commission yielded:—

Constituents.	G. S. Packer.	J. Pat- tinson.	E. Riley.	J. E. Stead.	Max. Diff.
Combined carbon ..	0.055*	0.034	0.036	0.035	0.021
Silicon ..	0.006	0.005	trace	0.008	0.008
Sulphur ..	0.030	0.030	0.023	0.036	0.013
Phosphorus ..	0.040	0.041	0.041	0.042	0.002
Manganese ..	0.275	0.310	0.258	0.317	0.059
Copper ..	—	—	0.025	—	—

The American Commission published (*Proc. Amer. Soc. of Civil Engineers*, vol. xxi., pp. 59-67) the following

* The high percentage of carbon reported by Packer is held to be due to the fact that the determination was effected in T. Brown and Co.'s laboratory in Sheffield, in the centre, that is, of a large works, and therefore in an atmosphere in which dust was always present, so that with the greatest care it was not possible to obtain concordant results. This fact indicates the great importance of maintaining a condition that is subsequently dealt with (favourable position of the laboratory).

results of phosphorus determinations in a series of steel samples:—

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
W. P. Barba ..	0.041	0.015	0.095	0.091	0.041
A. A. Blair ..	0.040	0.016	0.098	0.091	0.041
T. M. Drown ..	0.042	0.016	0.104	0.090	0.042
C. B. Dudley ..	0.040	0.016	0.099	0.097	0.039
P. W. Shimer ..	0.041	0.017	0.098	0.096	0.039
Maximum difference	0.002	0.002	0.009	0.007	0.003

Remarks. — Sample No. 3 contained an appreciable quantity of arsenic.

The differences in these analyses are, it is true, incomparably smaller than in the examples previously cited, and for many technical purposes may be disregarded. They are still, however, quite appreciable enough to have a disturbing influence, not only in purely scientific researches, but also in many instances in practice. The analyses are, however, it must not be forgotten, the careful work of special commissions, and not the average results of very busy works laboratories, from which equally careful analyses cannot well, as a rule, be expected, on account of the excess of work, almost all of which has to be disposed of in the shortest possible time.

In saying this I have no intention of decrying the value of ironworks laboratories. On the contrary, I desire to direct your attention to this point in order to show you that it is just these laboratories which at the present time, under the pressure of urgent necessity, have to conduct enormous numbers of analyses, and, besides this, have frequently to leave to others much more of the laboratory work than the chemists engaged there like—it is just these laboratories that do more work, and better work, than can reasonably be expected from them under these conditions.

Even small analytical differences, however, which unfortunately can in no way be regarded as rarities, frequently make themselves felt in an objectionable manner, not only in purely scientific researches, but also in many cases in practice.

Thus, for example, if a given composition or a given limit to the percentages of the various constituents is specified by the purchasers as a condition of acceptance, it is evident that even very small deviations in the analytical results may have disagreeable consequences. An instance that came under my notice will illustrate this. In an engineering works an order was given for boilers, the plates of which were specified not to contain more than 0.020 per cent of sulphur. The plates were supplied by an iron works, and in them 0.014 per cent of sulphur was found by the producer. As the limit of the contract was very short, the engineering works found it necessary to work the plates supplied on the strength of this determination, without waiting for the check-analysis required by the purchaser. The boilers were finished when the second analysis came to hand; but this yielded 0.034 per cent of sulphur!

Such examples, of which many might be cited, clearly show the urgent necessity of doing something to meet this evil, and the great importance of being able to be perfectly certain of the results yielded by chemical analysis. The result will show, and reference to it may not be out of place here, that more advantages will also accrue than would at first sight be imagined. If, for example, it were made absolutely certain that the limits of error of the determination of sulphur amounted to, say, ± 0.005 per cent, it is evident the works in question, in order to satisfy with safety the required conditions, could supply only such plates as were found to contain not more than 0.010 per cent of sulphur. As, however, it is only rarely that an ironworks is in a position to regularly produce a material with so low a percentage of sulphur, the immediate consequence would be that the purchaser would be compelled to raise proportionately the limits fixed for the allowable percentage of sulphur.

In what manner the investigations required for the solution of this problem can be, and will be, of still further practical use in this direction will be shown later.

The necessity of doing something in order to obtain standard—that is, concordant—analytical results has long been recognised, and in consequence endeavours in this direction have been made for many years past.

Thus, at the instigation of Dr. Dudley, in Altoona, Pennsylvania, an American Commission was formed, consisting of Messrs. Metcalf, Rodd, and Hunt of Pittsburgh, Barba and Blair of Philadelphia, Drown of Boston, and Shimer of Easton, with Mr. John W. Langley as President. This Commission, since the Chicago World's Fair, has worked in conjunction with the English Commission, consisting of Professor W. C. Roberts-Austen (President), Sir F. A. Abel, Bart., E. Riley, J. Spiller, G. J. Snelus, W. A. Tilden, and Thomas Turner, and with a Swedish Commission, consisting of Dr. A. Tamm, Professor C. G. Särnström, Dr. P. E. W. Öberg, Professor O. Pettersson, and R. Åkerman as President. Reports of the British Committee were published by the British Association in 1889, 1890, 1891, 1892, and 1893. Again, in Germany, chiefly by the initiative of the *Verein deutscher Eisenhüttenleute*, and of the late Dr. von Reis, a Commission was formed with similar objects, consisting of Messrs. Wolf of Dortmund, Giebsattel of Oberhausen, Corleis, Gerstner, and Salomon of Essen, and Becker of Rothe Erde, near Aix-la-Chapelle. Moreover, a number of eminent chemists have also for some years past been engaged on similar work, and their endeavours have been supported by premiums offered by technical societies.

In technical literature these endeavours are very noticeable. Thus, in the more recent works on iron analysis (Blair, Wedding, &c.), there is a growing attempt to present comparative criticisms of the various methods, and to study more exhaustively their sources of error.

I myself have been occupied with this work for many years past, and shall here merely refer to an article published in the *Oesterreichische Zeitschrift für Berg- und Huttenwesen* in 1884 on the accuracy of chemical analysis, and to my two larger treatises, "Praktisches Handbuch für Eisenhütten-Chemiker," 1885, and "Fortschritte im Eisenhütten-Laboratorium in den letzten 10 Jahren," 1895-96, in which not only are the causes of errors in analysis discussed generally, but special attention is also given to criticising the various methods.

At the fifth International Congress for the Unification of Methods of Testing, held at Zürich in September, 1895, the proposal was made by Dr. Wedding and myself, based on papers on the subject read by us, that support be afforded to an International Commission to deal with the solution of this problem, and the motion was carried by the Conference.

Turning now to the problem itself, it is evident that its solution must be preceded by an accurate knowledge of the causes that bring about differences in analyses, so that it is first necessary to consider the sources of error in chemical analyses.

Regarded from a general point of view these are—

1. Gross errors in the analysis.
2. Impure reagents.
3. Errors due to the apparatus, &c.
4. Errors due to the operations.
5. Errors due to the analytical methods.
6. Personal errors.
7. Errors due to differences in the calculation of the analyses caused by the values of the atomic weights on which they are based.
8. Want of homogeneity of the sample.

I trust that it will not be out of place to consider a little more closely these various sources of error.

1. Gross errors in the analysis, with which may also

be classed confusion of samples, errors in calculation, &c., should obviously never occur. Their occurrence is due to ignorance, want of skill, or carelessness on the part of the analyst, to defective equipment of the laboratory, and to overwork.

What can and must be done to obviate these errors is evident:—Employment of skilled analysts, diminution as far as possible of laboratory work, suitable equipment of the laboratory, and avoidance of overwork. At the same time, it may not be out of place to consider these points more closely, for now and again it is just in this direction that grave errors are committed. The analysis of steel is generally recognised to belong to the most difficult and most ticklish portion of chemical analysis, and should only be entrusted to skilled and reliable analysts. Moreover, it is, too, by no means the only duty of the ironworks' chemist to conduct his analysis according to known recipes, as in a cookery-book. Not only has he frequently to solve problems in which the known methods leave him in the lurch; but it is also under all circumstances his task, his duty indeed, to make as thorough a study as possible of new methods described in the literature of the subject. In this way his knowledge is widened, and the possibility is presented of introducing effective new methods, and of making it clear to himself what differences can arise by the employment of other methods than those he employs. He, however, has also an opportunity of so modifying new methods that they can be applied with distinct advantage to practical use. Anyone who is unable to test an analytical method thoroughly is unfit to be chemist in an ironworks laboratory.

Analytical chemistry, and not least the branches of it dealing with the investigation of iron and steel, has become so extensive and so progressive a science, that any frequent change of staff in ironworks laboratories is as far as possible to be avoided. For this reason the principle occasionally adopted of employing beginners in the metallurgy of iron in the laboratory, and after a time to find places for them in the works themselves, is to be condemned. It is certainly true that it is of considerable use to works officials if they have worked for some time in the works laboratory; but it must not be forgotten that the works laboratory is provided in the first place to conduct accurate analyses, and if it is also provided in the interest of the works, it is obviously an absolute necessity that the interests of the laboratory should be fully and completely preserved.

That in modern works laboratories a part of the work must be left to unqualified assistants is a matter for regret, which must be ascribed to the fact that an enormous number of analyses have to be got through as rapidly as possible. It is indeed true that there are such assistants who possess all the qualities for enabling them to carry out analytical work, if a skilled chemist is at hand on the one hand to check their work, and on the other to come to their aid in the case of need. Such assistants are, however, very rare, and on the other hand I have seen, in small works laboratories, where unqualified assistants work without supervision, things (such as determining silicon in grey pig-iron weighing the silica with the graphite, in determining tungsten in tungsten steel by fusing the silica and tungstic acid with potassium bisulphate, and extracting the fused mass with boiling water, &c.) which render it my duty to advocate most urgently the limiting, as far as possible, the employment of such assistants as these. Moreover, it is a well-known fact that the best and most certain methods, when they are currently used by these assistants, do not yield nearly such accurate results as in the hands of qualified chemists, and that the supervising chemist has constantly to guard against the introduction by the assistant in the course of time of slight carelessness in performing his duties.

(To be continued).

NOTICES OF BOOKS.

Nineteenth Annual Report of the Connecticut Agricultural Experiment Station for 1895. New Haven: Tuttle, Morehouse, and Taylor.

THE Connecticut Agricultural Experimental Station was established as far back as 1877. It analyses manures, cattle-foods, seeds, milk; identifies grasses, weeds, moulds, blights, mildews, useful and injurious insects, and gives information on subjects of Agricultural Science. It seeks to obtain for analysis samples of all the manures sold in Connecticut, and also samples of foods and drinks sold in the State, with reference to adulterations.

From the report of work done we learn that more than 22,500 tons of commercial manures are introduced yearly into the State, at the expense of more than 700,000 dols.

The law relating to the sale of manures makes the seller responsible for affixing a correct label to every package or lot sold or offered, as well as the payment of an analysis fee of 10 dols. for each fertilising ingredient which the manure contains or is alleged to contain.

The constituents whose determination is necessary are generally nitrogen, phosphoric acid, and potash. The fees are usually 10, 20, or 30 dols., according as one, two, or all of these ingredients exist in the manure.

A sealed sample has to be deposited with the Director of the Station by the manufacturer or importer, and a certified statement of composition must be deposited with him. A statement of the percentage of nitrogen, phosphoric acid, and potash, and of their states is required. The percentage of insoluble phosphoric acid may be stated or omitted.

The law of the State requires that every person in the State who sells any commercial manure, of whatever kind or price, must annually report to the Director of the Experimental Station, and on demand shall deliver a sample for analysis. Gypsum is, rather curiously, considered to come under the law as a "commercial fertiliser."

In the scale of values for the chief manurial ingredients we find nitrogen in ammonium salts valued at 18½ cents per lb.; in nitrates, 15; organic nitrogen in fish, blood, and mixed manures, at 16½ cents; in tankage, 16; phosphoric acid soluble in water, 6 cents per lb.; in dry ground fine fish, 5½; in mixed manures insoluble in ammonium citrate, 2 cents; potash as sulphate free from chlorides, 5½, and as muriate, 4½ cents.

Leather, whether in its untreated state, or steamed or roasted, is declared to be of no manurial value. Dried blood is found to be rich in available nitrogen.

Cotton-seed meal during the past season has been found the cheapest source of available nitrogen. It is as rapidly and fully available as the best forms of animal matter.

"Castor pomace" is a good manure, but very poisonous to stock.

Of the 78 brands of special manure tabulated in this report, 19 are below the manufacturers' guarantee in respect of one ingredient, and 10 in respect of two ingredients.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 3, July 20, 1896.

The Perpetual Secretary announces to the Academy the loss which it has sustained in the person of A. Kekulé von Stradonitz, a correspondent of the Chemical Section, who died at Bonn on July 13th, 1896.

Study of Lanthanum Carbide.—Henri Moissan.—Lanthanum oxide, mixed with carbon and heated in the electric furnace, readily produces a transparent crystalline carbide of the formula C_2La . This carbide is decomposable by water at the ordinary temperature, yielding a mixture of ethylene and of methane accompanied with traces of ethylene (?). The proportion of methane is a little higher than that afforded by cerium carbide. At the moment of its destruction by water this compound furnishes a very small quantity of liquid and solid carbides.

Electroscope with Three Gold Leaves.—L. Benoist.—With three leaves the angle of limit extends to 120° . The apparatus may thus serve for higher potentials without fear of the gold leaves being torn off.

On Metallic Alloys.—Henri Gautier.—This paper requires the two accompanying figures.

Oxy-Salts of Mercury.—Raoul Varet.—The author concludes that the oxy-salts of mercury follow strictly the law of thermo-chemical modules; that mercuric nitrate is in the state of a neutral salt in the midst of its nitric solutions; and that mercuric sulphate dissolved in an excess of sulphuric acid is in a state of an acid salt absolutely comparable to the corresponding potassium and sodium salts.

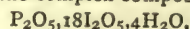
Action of Haloid Compounds of Phosphorus upon Iron, Nickel, and Cobalt.—A. Granger.—The results obtained are—

		Calculated as	
		Fe_4P_8 .	Found.
Iron		70'64	71'04
Phosphorus		29'36	29'44
		Calculated for	
		Ni_2P .	Found.
Nickel		79'20	79'09
Phosphorus		21'80	20'98
		Calculated for	
		Co_2P .	Found.
Cobalt		79'20	79'61
Phosphorus		21'80	20'43

Some Combinations of Iodic Acid with other Acids.—Paul Chretien.—The author has obtained and described the molybdo-iodic salts of sodium, of potassium, ammonium, and barium, and the free molybdo-iodic acid—



He has also produced metatungstic-iodic compounds of the general formula $I_2O_5(4WO_3)_m M_2O_n H_2O$. The phosphoiodic acid has the complex composition—



Action of Ammonia upon Potassium or Sodium Paratungstates.—L. A. Hallopeau.—The author's observations are a new proof of the dissimilarity existing between the chemical properties of the potassium and sodium paratungstates. The author has already shown that these bodies act in a different manner upon gelatinous zirconia, which dissolves on boiling in potassium paratungstate, but is insoluble in sodium paratungstate.

Action of Reducing Agents upon the Nitroso-compounds of Osmium.—L. Brizard.—The amidic chlorosmiate is a reducer. Its solution instantly decolorises permanganate in an acid liquid; in an alkaline liquid there is formed a maroon-brown precipitate. With mercuric chloride there is instantly formed in the cold a grey precipitate, which rapidly blackens. Cupric salts are reduced to the cuprous state.

Fermentation of Uric Acid by Micro-organisms. E. Gerard.—The author's experiments show that certain microbes existing in the air decompose uric acid and form urea.

Action of Sulphur Chloride upon Pentaerythrite.—J. Bougault.—This paper is not suited for useful abstraction.

Determination of the Congelation-point of Dilute Aqueous Solutions.—A. Ponsot.—Will be inserted in full.

No. 4, July 29, 1896.

Certain New Experiments relating to the Preparation of the Diamond.—Henri Moissan.—A new combustion was made of diamonds prepared in part by means of small cylinders filled with charcoal of sugar, and partly by means of metallic blocks of iron and copper. These two procedures furnished the purest diamonds. They sank in methylene iodide, scratched rubies with ease, and contained no black diamonds. The weight of the diamonds was 5.7 m.grms.; when burnt, they left a trace of ash, the weight of which could not be appreciated with the balance. We collected 20.5 m.m. of carbonic acid. Theory requires for 5.7 m.grms. 20.9 m.m. This substance therefore responds to the fundamental property of carbon, yielding for 1 grm. of substance 3.666 grms. of carbonic acid.

Study of the Black Diamond.—Henri Moissan.—We find in nature, both in Brazil and at the Cape, transparent diamonds containing inclosures of various forms. These inclosures may be of different nature, but the most numerous are black, and when abundant afford the variety of crystallised carbon of a fatty aspect which is known by the name of "black diamond." We are able to demonstrate that these black enclosed matters are due to a variety of carbon differing from the diamond in the following respects:—A black diamond of 2.2365 grms., presenting some small flaws, but transparent, was enclosed in a piece of cloth, placed on an anvil, and broken with the hammer. It was split at the first shock, and yielded very distinct pointed octahedra. We reduced the whole to fine powder in an Abich mortar, and this dust, of a blackish grey, is found under the microscope to be formed of fragments. We heat, then, about 1 centigram. of this powder in a tube of Bohemian glass traversed by a current of oxygen at a temperature lower by 200° than the temperature of combustion of the diamond. The experiment lasts half an hour. We observe very distinctly a slight escape of carbonic acid, which soon ceases, and which is shown by baryta water. After cooling, the diamond has lost its grey tint and has become white. The black matter which was contained in this diamond therefore burns in oxygen, yielding carbonic acid, and the diamond resumes its transparency. The experiment succeeds only with black diamond reduced to a very fine powder.

Homogeneity of Argon and of Helium.—W. Ramsay and J. Norman Collie.—(See p. 75).

Camphoric Mononitrile: its Anhydride and its Anilide.—A. Haller and M. Minguin.—The authors abandon the further investigation of this subject, as they find that they have to some extent been anticipated by Oddo and Leonardi.

Mean Density and the Specific Heat of Alloys of Iron and Antimony between 0° and 100°.—J. Laborde.—The author gives a table showing the quantity of iron contained in the alloys and obtained on analysis, the density of these alloys at 0°, and the specific heat calculated according to the composition. The numbers found for the specific heat are all greater than the numbers calculated according to the rule of mixtures, and the most important differences are much greater than experimental errors. The magnetic properties of these alloys increase abruptly when the proportion of iron reaches and exceeds that corresponding to Fe_3Sb_4 .

Study on the Nitrogen and the Argon of Fire-damp.—Th. Schlöesing, jun.—The author has sought for argon in the nitrogen of fire-damp, and has found 1.1 per cent—a proportion very close to that (1.19) which characterises the nitrogen of the atmosphere. He has next sought for argon in the coal of St. Etienne and of Plat-de-Gir, and found that they contain, if any, at most 1/200,000 of an element comparable to argon.

Cranial Endography by means of the Röntgen Rays.—MM. Remy and Contramoulins.—The authors have obtained endographic cranial proofs superior in distinctness to any produced hitherto. The superiority of these proofs depends, on the one part, on the use of the arrangement devised by M. Collardeau, and, on the other, to the remoteness of the source of light.

Preparation of Selenic Acid.—R. Metzner.—The author uses as his material selenious acid, oxidising it by means of permanganic acid obtained from barium permanganate.

On a New Cobaltite: Magnesium Cobaltite.—E. Dufau.—If we heat in the electric arc a suitable mixture of cobalt sesquioxide and of magnesia, oxygen is fixed, and the mixture is completely transformed into crystalline magnesium cobaltite, CoO_3Mg .

Solutions of Trichloracetic Acid.—Paul Rivals.—A thermo-chemical memoir, not well adapted for abridgment.

Vinyltrimethylene and Ethylenetrimethylene.—G. Gustavson.—The author obtains vinyltrimethylene by causing zinc powder and alcohol to act upon the tetrabromhydride of pentaerythrite $[\text{C}(\text{CH}_2\text{Br})_4]$. The combination of vinyltrimethylene with hydriodic acid leads to new substances. The alcohol and the ethylenetrimethylene derived from it have been obtained, but not specially studied. I have examined in detail the action of alcoholic potassa upon this iodide. We obtain again a hydrocarbon, C_5H_8 , but it is an isomer of vinyltrimethylene, boiling at 37.5°. Having regard to the manner of formation of this hydrocarbon, it must be regarded as ethylenetrimethylene.

Constitution of Pinacolone.—Maurice Delacre.—The author distinguishes Butlerow's acetone from pinacolone by the action of aqueous hydrobromic acid. He weighs in each of two stoppered bottles 35 grms. of one and the same concentrated solution of hydrobromic acid, and adds to each, suddenly, and without refrigeration, 10 grms. of the product. With pinacolone the liquid becomes homogeneous, blackish brown, heats, and gives rise in some time to an abundant deposit. With acetone, the mixture remains of a straw yellow, and even after eight days remains perfectly limpid without the slightest deposit.

Crystallographic Properties of some Alcoyl-camphors of the Aromatic Series.—J. Minguin.—This paper does not admit of useful abridgment.

Formation and Etherification of Crotonylic Alcohol.—E. Charon.—The author accentuates the curious fact that in the reduction of crotonic aldehyde the reaction considered as secondary, and yielding a pinacone, becomes the principal reaction with a yield of 60 per cent.

Electrolysis of Fatty Acids.—J. Hamonet.—The author has studied the electrolysis of potassium butyrate and isobutyrate.

NOTICE.

The STUDENTS' NUMBER of the CHEMICAL NEWS will be published on Friday, September 11th. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.

Advertisements for this Number should reach the Office not later than Wednesday, 9th Sept.

CITY AND GUILDS OF LONDON INSTITUTE.

SESSION 1896-97.

The Courses of Instruction in ENGINEER-

ING and CHEMISTRY at the Institute's Colleges commence in October, and cover a period of two to three years. The MATRICULATION EXAMINATION of the CENTRAL TECHNICAL COLLEGE will be held on September 21st to 24th, and the ENTRANCE EXAMINATION of the Day Department of the TECHNICAL COLLEGE, FINSBURY, on September 22nd.

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Professors:—O. HENRICI, LL.D., F.R.S. (Mathematics), W. C. UNWIN, F.R.S., M.I.C.E. (Civil and Mechanical Engineering), W. E. AYRTON, F.R.S. (Physics and Electrical Engineering), H. E. ARMSTRONG, Ph.D., F.R.S. (Chemistry).

CITY AND GUILDS TECHNICAL COLLEGE, Finsbury (Leonard Street, City Road, E.C.). The DAY DEPARTMENT provides Courses of Intermediate Instruction for Students not under 14 years of age, preparing to enter Mechanical or Electrical Engineering and Chemical Industries.

The ENTRANCE EXAMINATION will be held on September 22nd, and the new Session will commence on October 6th.

Professors:—S. P. THOMPSON, D.Sc., F.R.S. (Electrical Engineering), R. MELDOLA, F.R.S. (Chemistry).

JOHN WATNEY,
Hon. Secretary.

City and Guilds of London Institute,
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SESSION 1896-97.

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The SESSION extends from TUESDAY,

6th OCTOBER, 1896, to FRIDAY, 4th JUNE, 1897.

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DAVID LEWIS, Treasurer.

Treasurer's Chambers, 20, York Place,
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APPOINTMENT OF DEMONSTRATOR IN CHEMICAL DEPARTMENT.**The Council invite Applications on or before**

the 10th SEPTEMBER, 1896, for the above appointment, vacant in consequence of the appointment of Dr. Boyd as Lecturer in Chemistry to the Hartley Institution, Southampton. The duties will commence on October 1st, 1896.

Particulars of the stipend, conditions, and duties will be sent on application to the undersigned, to whom all applications for the appointment should be sent.

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NOTICE TO ANALYSTS AND LABORATORY DIRECTORS.**Best METHYLATED SPIRIT, manufactured**

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THE CHEMICAL NEWS.

Vol. LXXIV., No. 1917.

NITROGEN AND ARGON IN FIRE-DAMP, AND IN THE ROCHEBELLE GAS.

By TH. SCHLÆSING, Jun.

We have seen (*Comptes Rendus*, July 27, 1896) by what considerations I have been led to determine exactly the argon contained in the nitrogen extracted from fire-damp, and how I have proceeded in this determination. The following table summarises the principal conditions and the results of these experiments:—

	Pressure over which the fire-damp is evolved in c.c. of water.	Fire-damp having yielded N with argon.	N with argon ex- tracted from fire- damp.	Argon.	N with argon in 100 of fire-damp.	Argon in 100 of fire- damp.	Argon in 100 N and fire-damp.
	C.m. Litres.	C.c.	C.c.	A.	B.	C.	
Anzin	400	3'5	634'0	20'78	18'1	0'594	3'28
Bessèges	4 to 5	4'9	186'7	3'04	3'8	0'064	1'63
Firming	16	18'4	135'8	2'27	0'74	0'012	1'67
Liéven	70	5'5	437'1	9'71	8'0	0'166	2'22
Plat-de-Gier	75	1'9	592'9	10'85	30'0	0'601	1'83
Ronchamp	8	9'1	255'4	2'79	2'8	0'031	1'09
St. Etienne	600	15'5	497'5	5'81	3'2	0'037	1'17

The various samples had been taken without the accidental introduction of air. Before analysis I found, by means of phosphorus, that they were absolutely free from oxygen; an insignificant quantity of air introduced into the fire-damp was immediately seized by this reagent.

It is evident how laborious these analyses have been, especially when the fire-damp is very poor in nitrogen; in particular in the study of the fire-damp of Firming, which contains only 0'74 per cent of N. It was requisite to burn 18'4 litres (at 0° and 760 m.m.) of the gas obtained in order to obtain 135'8 c.c. of N, and ultimately 2'27 c.c. of argon. In spite of the material difficulties of the experiments the desirable precision was, I believe, realised. I give as a proof the following verifications. On two samples, which had led respectively to the smallest and the greatest value of the proportions of argon per cent of nitrogen and argon, I repeated the entire series of operations, and obtained:—

	Vols. at 0° and 760 m.m., fire-damp having yielded N with argon.	N with argon extracted from fire-damp.	Argon.	Argon in 100 N and argon.	Differ- ence.
	Litres.	C.c.	C.c.		
Ronchamp—					
1st determ.	9'1	255'4	2'788	1'092	0'006
2nd determ.	7'8	218'2	2'369	1'086	1'88
Anzin—					
1st determ.	3'5	634'0	20'779	3'277	0'013
2nd determ.	2'0	360'0	11'752	3'264	1'88

We have thus arrived the second time at the same results as the former within about $\frac{1}{100}$, and this with samples of fire damp in which the argon forms only $\frac{1}{100}$ or merely $\frac{1}{300}$. Argon, in virtue of its chemical inertia, can be determined (as we see) with a rare accuracy. Experimentalists should take every opportunity of taking up its determination, which cannot fail to be sometimes

highly instructive, instead of restricting themselves to qualitative recognitions.

I will add the figures yielded by another gas, obtained also from coal-beds, but quite different from fire-damp in its constitution. I speak of the gas evolved in the mines of Rochebelle with such dangerous force and suddenness, and which consists essentially, as is known, of carbonic acid. I have been able to make a complete analysis of it, from which results the following centesimal composition:—CO₂, 98'13; N (and argon), 1'14; CH₄, 0'73. The nature of the hydrocarbon here mentioned has been established with the eudiometer with perfect distinctness. I have also sought for argon in the gas of Rochebelle, and have found—

Vols. at 0° and 760 m.m. Gas of Roche- belle treated.	N with argon ex- tracted.	Argon.	N with argon in 100 of the gas treated.	Argon in 100 of the gas treated.	Argon in 100 of N and argon.
Litres.	C.c.	C.c.			
20'0	228'9	4'29	1'14	0'021	1'87

These results lead to various conclusions.

The argon, the presence of which I have shown in fire-damp, has been found in all the samples where I have sought for it. It exists also in the gas of Rochebelle. I have made the spectral verification in three samples from Anzin, Plat-de-Gier, and St. Etienne.

The percentage of nitrogen in fire-damp (column A) varies in the ratio of 1:40; in that of argon (column B) as 1:50. Nitrogen and argon are therefore met with in proportion which seem to have no relation with that of methane, the principal gaseous product derived from the materials of coal. This is an additional reason for placing the origin of the two gases outside the decomposition of these materials.

Whilst the nitrogen and the argon contained in 100 parts of fire-damp have undergone such wide oscillations, they have varied with reference to each other (column C) only in the proportion of 1:3; they seem in some manner connected together.

The percentage of 1'17 argon (or 1'18 after correction) in 100 nitrogen and argon, a proportion which characterises atmospheric nitrogen (1:19) which is found in the specimens from St. Etienne, examined the first in date, and whence was derived the idea of fossil air imprisoned for a long time in the coal, no longer presented itself in the sequel.

It is possible that the air has intervened otherwise, in a less direct manner, in the composition of fire-damp. It may have been introduced into this gas with the concurrence of water. Water saturated with air may have been able under certain conditions to give up to the fire-damp the gases which it held in solution. We should thus explain to ourselves that in fire-damp the percentage of argon in the mixture of nitrogen and argon rose above 1'19, a figure corresponding to the nitrogen of the air; for in the two gases dissolved in water the proportion is now 2'8, and in particular conditions it may reach 3'28. It would, in any case, seem very natural that water, which plays so great a part in the history of coal, should effect exchanges of gas with fire-damp. It would thus form that link, certainly very supple, the existence of which we trace between nitrogen and argon.

Further, the argon of fire-damp is not of necessity derived from the air. What is the source of argon on our globe? We do not know. Perhaps there exist in the depths reserves capable of diffusing it around them. It is known that Bouchard and Troost have found it along with helium in the mineral waters of Cauterets. Then Ch. Moureu has detected it, also with helium, in the waters of Maizières (*Comptes Rendus*, cxxi., p. 819). Thus argon seems generally diffused in the subterranean regions, as it is in our atmosphere. From this point of view the determinations of argon in the various gases escaping from the earth may yield verification of a high interest.

Whatever is the value of these hypotheses, there remain facts well established by the experiments above described: the presence of argon in fire-damp and in the gas of Rochebelle. There remain precise numerical determinations which may perhaps be of service to geologists.—*Comptes Rendus*, cxxiii., p. 302.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, August 11th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined by us all but one were found to be clear, bright, and well filtered.

There is again a serious deficiency in the amount of rain that should, according to the thirty years average, have fallen in the Thames Valley during the past month.

The average fall is 2.68 inches

The actual fall at Oxford.. 1.40 "

Deficiency 1.28 "

This makes the deficiency of rainfall to the end of July 5.66 inches.

The rainfall has been very unevenly distributed throughout the month; of the 1.40 inches measured, 0.82 in. fell on the 7th, the remainder, 0.58 in., being distributed over ten separate days.

Our bacteriological examinations give the following results:—

	Colonies per c.c.
Thames water, unfiltered	2731
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	46
Ditto ditto lowest	6
Ditto ditto .. (12 samples) mean	21
New River water, unfiltered	1886
New River water, from the Company's clear water well	22
River Lea water, unfiltered	2859
River Lea water from the East London Com- pany's clear water well	33

These results, like those of the chemical analyses given in the Tables, show that the quality of the water now being supplied to London is perfectly wholesome and of excellent quality.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES,
JAMES DEWAR.

CONTRIBUTIONS TO THE STUDY OF THE ANALYTICAL CHARACTERS OF THE COMPOUNDS OF TUNGSTEN.

By E. DEFACQZ.

ON resuming the study of some compounds of tungsten, and having need of a sensitive reaction to show the presence of tungstic acid, I have been led to take up the analytical study of the compounds of tungsten, and I am about to summarise this study.

We know that all the compounds of tungsten may be transformed either into tungstic acid or into an alkaline tungstate. It is also known that we may obtain an alkaline tungstate by fusing the metallic tungstates, soluble or insoluble, with an alkaline carbonate. The alkaline tungstates thus obtained are very numerous; certain of them undergo various transformations on dissolving them in water and submitting these solutions to prolonged ebullition.

Reagents give, with the solutions of different varieties of tungstates, precipitates whose physical characters and composition depend not only on the variety of the tungstate, but also on the conditions of temperature and solution in which the precipitation has been effected. There exists, however, a character common to all the varieties of tungsten by which we can recognise the presence of tungstic acid—the blue colouration obtained on adding to the dilute solution of an alkaline tungstate a fragment of zinc or of aluminium, and some drops of hydrochloric, sulphuric, or phosphoric acid. This reaction is not extremely sensitive.

Lucien Lévy has indicated the colouration due to the action of titanic acid upon some sulphuric solutions of phenols and of alkaloids; we have thought that tungstic acid might produce similar reactions.

The compound of tungsten is at first converted into tungstic acid; in most cases we may take the dry substance under analysis. We then treat this acid with four or five times its weight of potassium bisulphate and some drops of sulphuric acid, and heat gently. Under these conditions the tungstic acid dissolves. We then add so much sulphuric acid that the contents of the capsule do not solidify on cooling. We take a drop of this sulphuric solution, and add a drop of the reagent if liquid, or a few particles if it is solid; triturate for a few instants with the end of a stirring-rod, when we obtain colourations sometimes of an extreme intensity. We have tried the action of numerous organic bodies (carbides, alcohols, ethers, aldehyds, acetones, amines, phenols, alkaloids, &c.). The phenols and the alkaloids have given the best results.

On operating upon a drop of the sulphuric solution, as described above, we obtain with—

	Colouration.
Phenol	Very intense Saturn red.
Paracresol	Intense red-brown.
Thymol	Vermilion.
Hydroquinone	Very intense amethyst-violet.
Resorcin	Red-brown.
Pyrocatechine	Black-violet, sometimes black.
Pyrogallol	Red-black.
Naphthol (a)	Violet-blue.
" (β)	"
Salicylic acid	Very intense Saturn red.
Oxybenzoic acid (meta)	Feeble Saturn red.
" (para)	Nothing.
Quinine	Slight yellow.
Cinchonine	"
Morphine	Amethyst-violet, then brown.
Codeine	Rose, turning violet.
Conicine	Intense rose.
Solanine	Gamboge.
Veratrine	Intense sienna, then red-brown.
Aconitine	Yellowish brown.
Narceine	Yellowish green, then moss-green.
Picrotoxine	Orange-red, very intense.

In general these colourations are destroyed by water. Strychnine, brucine, nicotine, atropine, cantharidine, caffeine, santonine, pilocarpine, ergotinine, and hyoscyamine give no colouration.

Among these reactions we retain only the colourations given by phenol (red) and hydroquinone (violet), both from their intensity and the ease of procuring the reagent. These colourations easily detect the presence of $\frac{1}{100}$ to $\frac{1}{200}$ m.grm. of tungstic acid. — *Comptes Rendus*, cxxiii., No. 5.

THE INTRODUCTION OF STANDARD METHODS OF ANALYSIS.*

By the Baron HANNS JÜPTNER VON JONSTORFF
(Neuberg, Austria).

(Continued from p. 83).

It is obvious that the size and equipment of the laboratory must fulfil the given requirements. I can therefore confine myself to a few points which now and again are not sufficiently regarded.

The laboratory must be of sufficient size to utilise satisfactorily the working efficiency of those engaged in it, and to avoid confusion. The balance must be in a separate place. The situation of the laboratory should be so chosen that it suffers as little as possible from dust and vibration. It should therefore be placed neither immediately next to the street, nor too close to the works. It is decidedly open to objection to have a laboratory in a works, and the slight advantage thereby presented of convenient access from one to the other is not nearly enough to compensate for the drawback that in such a laboratory accurate results can never be obtained with certainty.†

For hygienic reasons the height of the laboratory should not be less than 13 feet, and perfect ventilation is requisite. Central heating of the laboratory is very desirable, more especially because the dust caused in the lighting and emptying of the stove is avoided. Gas is almost indispensable, and can, where coal-gas is unavailable, be easily supplied by a small oil-gas plant. I may also mention that the amount of work done in a laboratory is increased if there is no break in the middle of the day, the work being carried on continuously, and finished at a correspondingly earlier period. In this way opportunity is afforded the staff of obtaining free time for the relaxation so necessary after arduous laboratory work.

It is hardly necessary to state that overwhelming the laboratory with work should be avoided if trustworthy work is anticipated. A laboratory working like a factory is preposterous. And yet in this respect many are to blame. How is it possible to avoid errors and faults with excess of work in many cases almost inconceivable?

The demands here set forth in the interest of the laboratories (but also in that of the iron industry) will perhaps appear to many as exaggerated. If, however, it is desired to obtain really good and trustworthy analyses, they are not overstated at all. On the contrary, they are the indispensable preliminary conditions which, if unfulfilled, result in all subsequent work having but little value. Nevertheless, it can and will be replied that in all cases such painful accuracy is not required, and how can small works soar to the heights of the required installations?

Here, however, it is merely a question of alternatives.

In many cases the greatest possible accuracy is indispensable, and without it there is no certain agreement between the investigations of different laboratories. Where, however, it is desirable to have accuracy and agreement with other analysts (and this is very frequently

the case), the technical laboratory of an iron-works is a scientific establishment, and must be suitably provided as regards staff, space, time, and equipment.

Undoubtedly there are many investigations (especially the daily analysis for checking the working) in which such minute accuracy is not absolutely necessary, and for such purposes the demands may be considerably modified. If this is done, it must be clearly understood that it is no longer a question of a *chemical laboratory*, but of an *assay office*, and that the determinations thus obtained are not, as a rule, comparable with the results of actual chemical analyses. Where, too, chemical laboratories and assay offices are under the same direction, it is advisable to place them in distinct buildings, and not to employ the staff simultaneously in the two.

In this way it is possible to meet the requirements cited above. Any works, even the smallest, can have its assay office, if one of the managers will only give himself the trouble of superintending the work in it. Larger works, however, can and should have their own actual chemical laboratory, provided with a suitable staff and equipment. The comparatively small expense will certainly be well repaid. But small works, which are not in a position to provide and to maintain their own well-equipped laboratory, do best to have recourse to a neighbouring private laboratory of repute. In that way they fare better and cheaper than with a badly equipped laboratory of their own, which costs, it is true, very little, but which, from the inaccuracy of the work done, does more harm than good.

2. *The want of purity of the chemical reagents* is, as Dr. H. Wedding rightly remarked in his paper at the Zurich Congress, "most easily corrected by care on the part of the chemist before using the reagents." By paying careful attention to this point, very advantageous pressure will incidentally be brought to bear on those manufactories which produce reagents on a large scale. Nevertheless, testing the purity of the reagents is not always so simple as many imagine, and this, C. B. Dudley (*Journal of Analytical and Applied Chemistry*, 1893, p. 5), for example, has clearly proved when he says that, as a rule, blank trials are better than the purity tests, as an investigation of the reagents is often accompanied by most difficult manipulations, and it does not of itself clearly show how the impurities will affect the analysis.

3. *Errors due to the apparatus* include all errors in weighing and measuring, errors which are caused by neglecting to reduce weights and volumes to vacuum or to normal pressure and temperature, &c. Although these errors are more or less recognised, and are in many cases so small that they may be neglected, I venture at least to refer to them briefly, as every analyst has to assure himself as to their magnitude in order to be able to allow for them in cases where it appears to be necessary.

a. *Errors in Weighing*.—It is obvious that the balance employed should not be too sensitive nor too sluggish, and that the sensitiveness of the balance (a very important point in steel analysis) should be as nearly as possible constant with loads of various weights. On the other hand, the most perfect equality of the arms of the balance is not absolutely necessary, as both the substances to be weighed and the weights are always placed on the same side of the balance, and *absolute* accuracy of the weighing is in no way desired, as even in important determinations of percentage composition relative accuracy of the weighings perfectly suffices. This circumstance necessitates, however, that, at any rate in all cases in which considerable accuracy is required, all the weighings for one analysis must be performed on the same balance.

It is important that the terminal knife edges of the beam should be parallel to each other and to the central knife edge, as otherwise an accurate weighing is quite impossible. Thus, for example, with a balance made by an eminent firm, in which this condition was not fulfilled, two weighings of a small platinum crucible immediately fol-

* Read before the Iron and Steel Institute.

† See above, the remark in connection with Packer's carbon determination.

lowing one another gave a difference of 0.007 grm. (Jupner, "Praktisches Handbuch für Eisenhütten-Chemiker," p. 83).

Accuracy of the weights is similarly urgently required for obtaining correct weighings, but in this case, for the reasons previously given, relative accuracy suffices. In order to effect this a comparison of the separate weights is indispensable. Further, a testing of the graduation of the beam is not to be neglected.

In the course of time the weights, however, suffer changes, which, according to a Report of the German Commission (*Chemiker Zeitung*, x., p. 1481), may be ascribed mainly to the following causes:—

1. *Wear*.—As a rule, the wear is less in proportion to the smoothness of the surface, and therefore highly-polished weights are to be preferred to those with a dull surface.

2. Accumulation of foreign matter on the surface of the weights.

3. *Internal Oxidation*.—This takes place within the blowholes in the castings, and is considerably assisted by the penetration of salt solutions in the galvanic gilding or nickel plating. The weights, therefore, after the receiving of a galvanic deposit, should be repeatedly boiled in water, in order to remove the penetrated salt solution. Old weights that have become inaccurate by internal oxidation should, after re-adjustment, not be again gilded. Very small weights may advantageously be made, not of cast-brass, but of pieces of copper which have been obtained from a piece of electro-deposited copper, or from metal rendered compact by rolling and hammering.

The balance also suffers similar changes to the weights. Besides these permanent changes, however, there are temporary changes, which may briefly be discussed.

The length of the balance-beam may be changed unequally by heating. The weighing of warm substances should therefore be avoided, and care should be taken to avoid any one-sided heating of the balance, whether it be from a gas or petroleum lamp placed nearer to one beam than to the other, or whether it be merely from sunlight reflected from a window-pane. For this reason, as well as a protection from disturbing currents of air caused by breathing, weighings should be conducted only with closed balances. The balances made by A. Ruepprecht, Vienna, in which all the weights under 1 grm. can be placed in position with the case closed, are for these reasons deserving of much commendation.

According to R. Hennig (*Zeitschrift für Instrumentenkunde*, v., p. 16) air currents may also be induced when liquids are weighed in wide vessels owing to their evaporation, which may result in an alteration of the point at which the balance comes to rest. An error in weighing, which amounted to 0.4 m.grm., resulted in one such instance, and this could only be eliminated by determining the zero point of the balance immediately after the weighing, and without removing the liquid from the balance case. The presence of a substance which will absorb the vapour increases the error, such as calcium chloride or sulphuric acid in the case of moisture. The zero point of the balance may, too, be changed by an electrification of the balance supports, after rubbing one side with a cloth, or by frequent lightly-applied friction, such as moving backwards and forwards a box of weights on the cover of the balance case. Similar errors may also be induced, according to the observation of the German Commission (*Chem. Zeit.*, xii., 494), in removing glass or quartz weights from the box by their rubbing against the cloth lining, and so becoming electrically charged.

The condensation of moisture, or even it may be the accumulation of a denser gas layer on the surface of dry non-hygroscopic bodies, induces further errors in weighing, especially in the weighing of U-tubes, &c. Thus G. Papasogli (*L'Orosi*, x., p. 109; *Chemisches Centralblatt*, xvii., p. 559; Fresenius, *Zeitsch. f. Anal. Chem.*, 1888, p.

642) found that various powdered substances, which had been dried over sulphuric acid, increased in weight during the period of weighing (from three to six minutes) by from 0.001 to 0.003 grm.

When closed vessels are to be weighed, care must also be taken that the air enclosed in them has the same temperature and pressure as the surrounding atmosphere.

It has further been shown by T. E. Thorpe (*Journ. Chem. Soc.*, xlvii., p. 116) that the zero point of the balance is subject daily to slight variations, just as if one arm of the balance expanded somewhat more during the course of the day than the other.

β. *Errors in Measuring*.—It is of course evident that the various measuring vessels must be examined as to the correctness of their division and their relative agreement with each other. As a rule, an error of 0.1 per cent of the volume to be measured may in such cases be tolerated, although in especially important cases it will be necessary to take into calculation the exact volumes, for which reason it is advisable to provide correction tables for the measuring vessels that are used.

In reading off the volumes errors may also be made—errors in reading off—which may in part be parallax errors, and in part be due to errors made in estimating portions of the divisions into which the measuring vessel is subdivided. Various methods have been proposed for diminishing the first of these errors (mirrors, floats, &c.). With the necessary practice the parts of one subdivision of the measuring vessel may be estimated to within about one-tenth of a division (the error is about ± 0.1), and in all cases it may easily be estimated to within a quarter of a division.

Other errors result from the adhesion of the liquids to the sides of the vessel, and also in the way they are allowed to flow out, the mere reference to which will suffice.

γ. *Omitting to take into Consideration the Reduction of the Weights to Vacuo*.—According to the principle of Archimedes, every body which is plunged into a liquid or gaseous body loses so much of its weight as is equivalent to the weight of the body it displaces. This naturally leads to errors in the results of weighings; and although in many cases these are so slight that they need not be considered, yet occasionally they reach such an important amount that it appears desirable to take them into consideration.

For ordinary atmospheric conditions (height of barometer, temperature, degree of humidity), for the reduction of the weights to *vacuo*, the following formula holds good:—

$$P = p [1 + 0.0012 (\frac{1}{s} - 0.12)],$$

in which P is the weight in *vacuo*, p the weight on the balance, and s the specific gravity of the body to be weighed. It is assumed in this that the weights were of brass (sp. gr. 8.4).

Some examples may serve to show the differences between the weights in air and in *vacuo*:—

For ignited ferric oxide (sp. gr. 5.12) the formula shows $P = p (1 + 0.000096)$, that is to say, a difference in weight of about 0.01 per cent; for alumina, which has been heated to redness, with a sp. gr. of 3.85, the formula yields $P = p (1 + 0.000168)$, a difference in weight of 0.017 per cent; for magnesium pyrophosphate (sp. gr. 2.40, $P = p (1 + 0.00036)$), or a difference of 0.036 per cent; and finally, in the case of silica, sp. gr. 2.20, $P = p (1 + 0.000396)$, that is to say, a difference of about 0.040 per cent.

While, then, in almost every case no correction need be made for ferric oxide and alumina, in the two last cases mentioned under certain conditions somewhat important differences may result, as, for instance, about 0.01 per cent in the analysis of magnesite, of 0.036 per cent for calcined magnesite, and of 0.006 per cent in the analysis of a ferro-silicon with 14 per cent of silicon.

If platinum weights are used for the weighing, as is usually the case with the small quantities of substances

commonly used for analysis, the differences become somewhat larger. The reduction formula is then—

$$P = p[1 + 0.0012(\frac{1}{3} - 0.05)],$$

and one obtains therefore, in the cases above given, the following results:—Ferric oxide, $P = p(1 + 0.00018)$ —difference in weight = 0.018 per cent; alumina, $P = p(1 + 0.00025)$ —difference in weight = 0.025 per cent—magnesium pyrophosphate, $P = p(1 + 0.00044)$ —difference in weight = 0.044 per cent; silica, $P = p(1 + 0.00048)$ —difference in weight = 0.048 per cent. The analysis differences are consequently as follows:—In the case of magnesite $\Delta = 0.013$ per cent; with calcined magnesite, 0.044; and with 14 per cent ferro-silicon, 0.007 per cent.

The errors induced by this are, it is true, not very important, but they deserve to be considered in accurate work, especially in the presence of other sources of error which are similar in their effects, such, for instance, as the very marked solubility of magnesium pyrophosphate.

These conditions must, however, also be considered from another point of view. As a rule, the weights used for quantities exceeding 1 gm. are of brass, but of platinum for fractions of a gm., and finally the riders are made of aluminium. If these weights are entirely concordant in air, this is not true of their weights as reduced to *vacuo*. As a rule, the weighings of the original substance, if they exceed 1 gm., are, however, made with brass weights, but in the subsequent weighings of the much smaller quantities to be dealt with during the course of the analysis platinum weights are employed. The result is that the total weight of the several constituents can never agree exactly with the weight originally taken for the analysis, which in reality it ought to do.

(To be continued).

NOTES ON THE ELECTROLYTIC DETERMINATION OF IRON, NICKEL, AND ZINC.

By H. H. NICHOLSON and S. AVERY.

THE experimental part of this work was undertaken in the spring of 1892. During the progress of the work various articles on the electrolytic department of these metals have been published. Some of these investigations are closely related to those carried out by us. As, however, they differ in some important particulars, and as some observations have been made which, so far as we are aware, have not as yet been reported, it seemed well to present the results obtained although some parts of the work are still incomplete.

In the method of manipulation, free use was made of the text-books of Classen and Smith. A number of cells of the Grove-Tyndall form furnished the current. The current was controlled by means of a rheostat-box. The ampère was determined by means of a "Weston" voltmeter. The metals were deposited in platinum dishes of 300 c.c. capacity.

In no case was any attempt made to separate metals by careful regulation of the voltage, as the practical utility of such methods may be doubted till the literature of the subject is more copious.

I.—The Electrolytic Department of Iron.

The method of Classen and V. Reiss (*Ber. d. Chem. Ges.*, xiv., 1622) for the determination of the metals in their double oxalate solutions, a method which gives such admirable results in most determinations, cannot be applied with the same degree of convenience to iron, as a strong current and a hot solution are necessary.

Smith and Muir (*J. Anal. Chem.*, v., 488) found that iron is very readily precipitated from ammonium tartrate solutions containing free ammonia. They found, how-

ever, that under such circumstances the iron contains carbon. Still tartrate solutions seemed to offer possibilities for quantitative determinations sufficient to warrant a fuller investigation of the subject.

Six grms. of tartaric acid were dissolved in water and added to a solution of ferrous sulphate. The solution was then diluted to 150 c.c. and rendered strongly alkaline with ammonia. The solution was then placed in a platinum dish, submitted to the action of a current of 0.115 ampère and 4 volts for six hours.

Taken, 0.0477 gm. iron. Weight found, 0.0476 gm. iron.

After weighing, the precipitate was dissolved in dilute sulphuric acid. A trace of the odour of hydrocarbons was present. The solution was then oxidised, precipitated with ammonia, and determined in the usual gravimetric way. The weight of the iron oxide corresponded to 0.0465 gm. of iron. The carbon present evidently compensated for the weight of the unprecipitated iron.

The following determinations were made in a similar manner:—

No.	Current.	Time.	Solution.	Iron taken.	Weight found.	Carbon by difference.
	Ampère.	Hours.		Grm.	Grm.	Grm.
1.	0.185	4	Strongly alkaline.	0.0620	0.0418	—
2.	0.115	14	Strongly alkaline.	0.0476	0.0487	0.0011
3.	0.115	6	Slightly alkaline.	0.0291	0.0294	0.0003
4.	0.5	5	Strongly alkaline.	0.0476	0.0492	0.0018
5.	0.5	5	Strongly alkaline.	0.0351	0.0364	0.0013

These figures show that strong currents and free ammonia are favourable to the precipitation of carbon. Hence attention was turned to the electrolysis of iron in neutral ammonium tartrate solutions.

To 25 c.c. of an iron sulphate solution, sodium hydroxide was added till the greater part of the iron was precipitated. A dilute solution of tartaric acid was now added till the greater part of the precipitate was dissolved; 5 grms. of ammonium tartrate were added and the whole diluted to 150 c.c. The solution made up in this way was found to be exactly neutral to litmus. It was necessary to employ a stronger current than when free ammonia was present. The following determinations were made:—

No.	Current.	Time.	Iron taken.	Weight found.	Iron calculated from Fe_2O_3 .
	Ampère.	Hours.	Grm.	Grm.	Grm.
1.	0.4	6	0.0630	0.0634	—
2.	0.4	6	0.0630	0.0635	—
3.	0.5	4½	0.0630	0.0626	0.0620

In all cases carbon was detected in the precipitated iron.

Attention was next given to the determinations of iron in sodium tartrate solutions. In some cases free sodium hydroxide was present. The sodium salt conducts the current much better than the ammonium salt. The precipitation of iron proceeds satisfactorily for a time. After a little black spots appear. When a strong current is employed, a white precipitate of ferrous carbonate forms on the deposited metal. Currents of 2 to 4 volts and of 0.05 to 0.1 ampère were employed to effect the separation of the iron from the solution. Towards the end of the precipitation carbon deposits rapidly. Vortmann (*Chem. Centrbl.*, 1893, 1070), by using currents of low voltage and precipitating the iron in fractions on weighed electrodes, seems to have avoided some of the unfavourable conditions above described. However, the general department of iron in sodium tartrate solutions was so unpromising that the investigation was not carried further in this direction.

The question now presented itself:—"Is the precipitation of carbon with iron peculiar to tartrates, or may we expect it when other organic compounds are present?"

To answer this question, a number of qualitative tests were made by adding to the iron solution, before passing the current, solutions of sugar, alcohol, glycerol, or of

salts of formic, acetic, lactic, citric, succinic, or benzoic acids. The currents employed were of the lowest voltage and ampère sufficient to give a deposit of several m.grms. in the course of an hour. As ammonium oxalate gives no precipitate of carbon under any circumstances, so far as we are aware, this reagent was used to hold the iron in solution when necessary. The iron was used in the form of ferrous sulphate.

When formates were present in the absence of other organic compounds, no trace of carbon could be detected in the precipitated iron. In all other cases the precipitated iron contained carbon. In the case of citric acid a quantitative determination was made.

A solution of ferrous sulphate containing 5 grms. of citric acid in the form of sodium and potassium salts with a little free acid was submitted for fourteen hours to a current of 0.2 ampère.

Taken, 0.0726 gm. iron. Weight found, 0.0740 gm. iron.

The absence of carbon in the case of oxalates and formates is explained by the fact that these compounds break up under the influence of the current, giving off all carbon, in the form of its highest oxidation product, i.e., carbon dioxide.

In all cases the amount of carbon deposited was increased by the employment of stronger currents, but in no case was it possible to obtain a precipitate free from carbon, except in the case of formates and oxalates, when organic matter was present.

Determination of Iron in Solutions containing Ammonium Oxalate and Sodium Borate.

We found that a slight modification of Classen's method greatly facilitated the precipitation of iron. The following gave satisfactory results:—

Twenty-five c.c. of a solution of ferrous sulphate were taken, 5 grms. of ammonium oxalate were added and brought into solution by the aid of gentle heat. Five c.c. of a saturated solution of borax were now added, and the entire solution diluted to 150 c.c. A current of 0.02 ampère was allowed to act on the cold solution for sixteen hours. Towards the end of the operation the anode became covered with a slight brown coating. A slight brown deposit also appeared on the dish above the iron deposit. The following method was used to dissolve these deposits:—Water was added until the surface of the liquid was raised above the brown deposit in the dish. The positive electrode was then brought in contact for a moment with the side of the dish, thus short-circuiting the battery and generating considerable heat in the electrodes. This had the effect of liberating and dissolving the brown deposit. The current was allowed to act for half an hour longer, when the dish was removed from the circuit, washed, dried, and weighed.

The precipitate was perfectly adherent, and showed no tendency to oxidise when washed with alcohol and ether. The following is a tabular statement of the results obtained:—

No.	Ammonium oxalate. Grms.	Saturated borax solution. C.c.	Current. Ampère.	Time. Hours.	Iron taken. Grm.	Iron found. Grm.
1.	5	5	0.02	16	0.0938	0.0933
2.	5	10	0.02	17	0.0938	0.0935
3.	6	10	0.06	4	0.0938	0.0938
4.	5	5	0.072	2	0.0938	0.0939
5.	6	5	0.125	2	0.0938	0.0938

It will be seen from the above that the presence of borax facilitates the precipitation of iron in ammonium oxalate solutions. The cause of the appearance of the slight brown deposit and the extent to which it might cause an error in results will be investigated later.

II.—The Determination of Nickel.

The determination of nickel presented no difficulties. The greater part of the experiments with iron were per-

formed in an analogous way with nickel; in no case was carbon deposited with the nickel. When iron and nickel are deposited together as an alloy in the presence of organic compounds the nickel does not prevent the contamination of the precipitate with carbon.

III.—Determination of Zinc.

Nearly all the published methods for the electrolytic determination of zinc give fairly satisfactory results. The tendency of the metal to be deposited in a spongy condition and the liability to oxidation are the principal difficulties usually encountered.

The tendency to oxidation may be prevented by the presence of formic acid in the solution, which by the liberation of hydrogen with the metal exercises a reducing action.

By the electrolysis of zinc formate in the presence of formic acid, Warwick (*Zeit. Anorg. Chem.*, i., 291) did not succeed in obtaining a complete deposit. The deposit is greatly influenced by the presence of sodium formate in the solution.

To a solution of zinc sulphate 3 c.c. of formic acid were added, and the solution partially neutralised with 1 gm. of sodium carbonate. The entire solution was diluted to 150 c.c. and placed in a current of 0.02 ampère for three hours.

Taken, 0.0611 gm. zinc. Found, 0.0603 gm. zinc.

In a similar manner the following determinations were made:—

No.	Formic acid. C.c.	Sodium carbonate. Grm.	Current. Ampère.	Time. Hours.	Weight taken.	Weight found.
1.	4	1.5	0.125	3	0.0611	0.0612
2.	5	1.0	1.000	3	0.0611	0.0611
3.	5	1.0	0.050	3	0.0611	0.0611

The deposit adhered well, was compact and evenly distributed on the surface of the dish; the colour was light grey, in some cases almost metallic in lustre. As will be seen from the figures, a considerable variation in the strength of the current is allowable. This method is not allowable in the presence of the metals of the hydrogen sulphide group, as well as in the presence of iron, nickel, and cobalt.—*Journal of the American Chemical Society*, xviii., No. 7, July, 1896.

THE PRACTICAL USE IN THE CHEMICAL LABORATORY OF THE ELECTRIC ARC OBTAINED FROM THE LOW POTENTIAL ALTERNATING CURRENT.

By MILO S. WALKER.

In this paper the author does not claim to have discovered any action of the electric arc that is not already known to chemists, but he will attempt to give a few suggestions as to the way in which the highest temperature at our command can be obtained and used in every chemical laboratory supplied with a fixture for incandescent lighting. Many colleges and secondary schools are equipped with these fixtures, and others can obtain them at but little cost. There is no practical reason why they should not be used for some experiments that cannot be performed with a Bunsen burner or a blowpipe.

The alternating current of about 50 volts and 1 to 5 amperes, now generally used for incandescent lighting, furnishes an excellent arc for chemical experimentation. It is very efficient, and can be handled easily and safely even by beginners in laboratory work.

The apparatus required consists of an iron or wooden stand, a screw clamp like those used for holding burettes, insulated copper wire, some electric light carbons, and a rheostat.

A piece of the so-called 10-ampère flexible lamp-cord

may be connected at one end with a plug set into the socket intended for an incandescent lamp. The two parts at the other end of the twisted cord are left free. Besides the lamp-cord, two pieces of ordinary insulated copper wire of medium size (about No. 20) and 70 c.m. long will be needed. These wires can be supplied and fixed as directed by any dealer in electrical supplies.

The rheostat is the most important part of the apparatus. Any commercial rheostat capable of carrying 12 amperes will answer all ordinary purposes. It may be necessary in large buildings, where one transformer supplies 100 lights or more, to use an additional resistance. About 40 feet No. 13 German silver wire has been found very satisfactory in a building where 175 lights are used.

The adjustable rheostat is essential to the proper control of the current, and to prevent too high heating of the wires and consequent melting of the safety fuses when the arc is started. All the experiments are started with a high resistance which is lessened until the proper arc light is obtained.

The assorted carbons are $\frac{1}{4}$ to $\frac{1}{2}$ inch in diameter. The cored carbons are much better than the ordinary uncored ones. For obvious reasons "coppered" carbons should not be used. Carbons differ much in quality. Some contain considerable quantities of carbides and carbonates of metals. Those manufactured for use in optical projection usually contain less of these substances and give the best results.

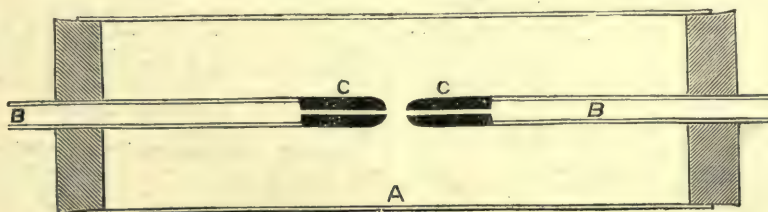
The operator should not touch any metallic fixtures connected with the earth while he is working with the apparatus, as serious shocks may be received if the transformer is not properly insulated, a defect not uncommon in electrical work. It is better to work at a table on which there are no gas or water fixtures. Gas should be conducted to the table by a rubber tube connected with a gas-cock so far removed that there is no danger of touching any part of the apparatus and the gas-cock at the same time. There seems to be no other danger in working with the 50-volt alternating current. The students

c.m. Fix into a wooden clamp, and connect with insulated wire like the other carbon. On account of the heat an iron clamp with insulated handle is better for some experiments. Connect all wires so that the circuit will be completed if the carbons are allowed to touch each other. As the light is intense the eyes should be protected by a dark or blue glass. The longer carbon is stationary. The movements of the shorter carbon are controlled like a test-tube and holder. The rheostat should be adjusted so that an arc $\frac{1}{8}$ to $\frac{1}{4}$ inch long can pass between the lower end of the longer carbon and the edge of the conical cavity in the smaller carbon. A small piece of the substance to be tested can be placed in the cavity. Most minerals and common metals fuse easily. A piece of quartz 2×1 m.m. fuses completely. A piece the size of a pea fuses on one side.

As this contribution is intended only to show how the electric arc can be obtained and used in a chemical laboratory, a description of experiments is omitted, except where they show the method of working. The apparatus has not been in use long enough to show all its possible applications, or even a small part of them. But it has been shown that many of the remarkable experiments of Moissan can be repeated on a smaller scale by this simple apparatus. His work suggests much that can be done in the ordinary chemical laboratory lighted by "incandescent lamps."

If iron, copper, or manganese ores are placed in the conical cavity, the metals are formed containing small quantities of carbides.

For reduction of oxides it is better to substitute for the solid upper carbon, a carbon tube made by removing the core from the "cored carbon" 3 or 4 c.m. long. This tube is then fastened into a brass tube of about the same outside diameter, but with a large bore. The joint can be made gas-tight by a paste of pure graphite and water. The brass tube is fixed and connected with wire like the upper carbon in the other apparatus. The end of the carbon tube should occupy the position of the lower end of the larger carbon as indicated above. Now a gas can



working in this laboratory sometimes receive shocks, but they generally consider shocks less disagreeable than accidental burns incident to work in general chemistry.

The electric arc can be used for the following purposes:—

1. To show the effect of high temperatures upon difficultly fusible and "non-volatile" substances.
2. For reduction of oxides of metal.
3. As a partial substitute for the blowpipe in qualitative analysis.
4. For the synthetic preparation of some compounds of carbon from the elements.

There is a wide range of experiments showing the effect of the electric arc upon substances almost infusible by other means.

The apparatus can be arranged in a variety of ways depending upon the experiment. For general use it may be arranged thus:—Fasten a cored carbon, about 10×1 c.m., in a vertical position so that the lower end is about 10 c.m. from the top of the table. Connect by wrapping with insulated copper wire, stripped where contact is made with the carbon. Bore a conical shaped cavity 4 or 5 m.m. deep in one end of another piece of cored carbon 4×1

be passed through the carbon tube so that it will strike a substance in the cavity of the small carbon while the arc is passing. Hydrogen or coal-gas may thus be conveniently used to prevent oxidation of metals while cooling; and seem to assist in reducing oxides and chlorides while the arc is passing. If carbon dioxide is used, carbon monoxide is formed with apparent increase in the reduction of oxides. In all these experiments a crater is gradually formed, and the arc generally passes from the inside of the carbon tube, thus giving maximum efficiency. When oxygen is used, the crater forms rapidly and enlarges to the full diameter of the carbon. Carbon monoxide is the main product of the quite rapid combustion, and acts as a powerful reducing agent upon an oxide in the cavity of the other carbon. By reducing with carbon monoxide in this way, and cooling in hydrogen, quite pure manganese has been obtained from pure manganese dioxide. Similar experiments with oxides of other metals will be tried as soon as pure materials are secured.

Experiments with the electric arc are particularly interesting to the student, because he is able to get quick, sharp, and definite results. The manipulation is so easy

that young students can obtain beads of copper, iron, or manganese after a few minutes' practice. The electric arc has been used in this laboratory as an aid in qualitative analysis and a partial substitute for the blowpipe, but the method will not be described at present because it has not been sufficiently tested. A special apparatus has been used in which the electric arc is inside a partially closed glass tube, and the volatile constituents of the substance to be treated are collected and partially separated on the sides of the glass. The results so far obtained are very satisfactory.

Some experiments on the synthesis of the hydrocarbons from their elements have been tried. Thus acetylene is easily prepared by the method of Berthelot (*Comptes Rendus*, liv., 640) modified by Dewar (*Proc. Roy. Soc.*, xxix., 188).

The apparatus may be made as follows:—

Fit a gas tight cork into each end of a straight lamp chimney. Pass brass tubes 1 c.m. diameter and 15 c.m. long through each cork. Into one end of each tube fix a tube of carbon 3 c.m. long, prepared and fitted as shown under experiments for reduction of oxides. The joints of carbon and brass tubes should be gas tight.

Fit the corks and brass tubes so that the ends of the carbon tubes are nearly together, test the apparatus for gas leakage, turn on the current and again test after the heat has reached a maximum. If air-tight pass a stream of hydrogen through the brass and carbon tubes. After the oxygen in the apparatus has been consumed it may be necessary to increase the current.

As there is nitrogen in the air from the apparatus, small quantities of hydrocyanic acid are formed at first along with acetylene. The yield of acetylene is not large, but the method seems to be fully as satisfactory as the usual laboratory method of preparation of this gas from coal-gas by burning it in an insufficient supply of air. This is recommended as a laboratory method for students. It is the only experiment showing synthesis of carbon and hydrogen from the elements, and the construction and manipulation of apparatus are not too difficult for any one who has had a few weeks' experience in a laboratory. — *American Chemical Journal*, vol. xviii., No. 4.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 18th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. J. K. Burbridge and James Proude were formally admitted Fellows of the Society.

A certificate was read for the first time in favour of Mr. Hugh Manners, Academy House, Airdrie, N.B.

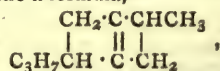
Dr. Tate was reinstated as a Fellow of the Society.

The following were duly elected Fellows of the Society:—Messrs. Robert Addie, John Caley, Charles Matthew Crossmann, B.Sc., Llewellyn John Davies, Leon Felix Goldstand, LL.D., Ralph Hamilton Hanger, Frederick William Harris, Ernest George Hill, B.A., Joshua Arthur Hughes, John Burnett Knight, Herbert E. Law, William Arthur Finch Lethbridge, B.A., Cecil Rudolf Lidgley, Percy Sykes Marshall, William McConnell, jun., Loxley Meggitt, Asutosh Rai Bahadur Mitra, James Stanley Muir, B.Sc., James Hadden Overton, Hastings Montague Page, Arthur Payne, Sigmund Georgjewitsch Rosenblum, Samuel Thomas Skelton, George Egerton Scott Smith, Douglas Stuart Spens Stuart, B.Sc., James Whitehead.

Of the following papers those marked * were read:—

*75. "The Action of Bromine on Pinene with reference to the Question of its Constitution." By W. A. TILDEN, D.Sc., F.R.S.

Experiments made by the author in 1888 led him to believe that pinene combines not only with two atoms, but with four atoms of bromine. This conclusion was confirmed by the independent experiments of Stschukareff in 1893. Wallach, however, maintains that pinene can unite with only two atoms of bromine, and the various formulæ proposed by different chemists for this hydrocarbon are based on that assumption. The author has, therefore, undertaken a fresh inquiry, as the result of which he is confirmed in his original opinion that pinene combines directly with four atoms of bromine, the amount of bromine entering the molecule by substitution for hydrogen being comparatively insignificant. He therefore proposes for pinene a formula,—



derived from a ring of six carbon atoms with a double para-linkage, the disruption of which at once gives a cycloid closely related to benzene, and accounts for the ready formation of cymene, &c.

*76. "Preliminary Note on some Products from Pinene Tetrabromide." By W. A. TILDEN, D.Sc., F.R.S., and A. NICHOLLS.

The liquid tetrabromide formed by the addition of pinene to four atoms of bromine, as described in the preceding paper, is a very unstable compound, for it begins to evolve hydrogen bromide soon after its formation if kept at or near the temperature of the air. In order to investigate the products of this decomposition, a considerable quantity of the bromide was prepared. From the resulting colourless solution the carbon tetrachloride was distilled by a water-bath, and the residual liquid subjected to distillation alone with the object of expelling as much as possible of the hydrogen bromide, which escaped for the most part as gas. A colourless distillate was obtained, leaving a small quantity of a brown oily residue, which boils at a high temperature with further decomposition. On re-distilling the perfectly colourless distillate under pressure reduced to about 10 m.m., it came over between 125° and 175°, leaving a small additional quantity of the dark residue, from which, after standing a few hours or days, a crystalline substance was deposited, which was identified by analysis and melting-point as Wallach's dibromide, $\text{C}_{10}\text{H}_{16}\text{Br}_2$, m. p. 169–170° (*Annalen*, cclxiv., 7).

In order to decompose the last portions of bromide in the distilled liquid, it was heated with excess of aniline to the boiling-point of the latter, and subsequently steam distilled. The distillate, acidified with dilute sulphuric acid in order to fix the small quantity of aniline present, and again steamed, gave a colourless hydrocarbon lighter than water. By fractionation, this was found to yield a portion boiling at 155–157°, which contains solid camphene crystallisable by cooling. The larger part comes over between 158° and 162°, and deposits no solid at –15°. Smaller fractions up to 185° were obtained, and these remain to be examined. The chief fraction, 158–162°, reduced aqueous solution of permanganate at 16–18°, and fixed a quantity of bromine corresponding approximately to Br_2 for C_{10} .

As with the quantity of hydrocarbon at our command it seemed improbable that a fraction could be separated in a pure state, it was thought best to submit the liquid to oxidation. Two portions, the product of one preparation of bromide, were taken, namely, 30 grms., boiling between 155° and 160°, from which the camphene had been frozen out as completely as possible, and 30 grms. boiling between 160° and 170°. Oxidation with aqueous permanganate at a temperature which never rose above 26° gave the same chief product, and the two products were therefore supposed to contain a common ingredient. The unchanged hydrocarbon and precipitated oxide of manganese having been removed, the clear solution was mixed with a quantity of sulphuric acid calculated to

neutralise the alkali contained in it. A white cloud made its appearance, which was removed on shaking with ether. The ethereal extract, submitted to distillation, left a watery residue, in which floated a nearly colourless oil of about the same density as water. The 30 grms. of hydrocarbon at $155-160^{\circ}$ gave 7.5 grms. of this fluid, and the 30 grms. at $160-170^{\circ}$ gave 6 grms. This substance is a well-marked acid, having a sour and astringent taste; it decomposes carbonates, and when mixed with solutions of soda develops much heat. Distilled under a pressure of 20 m.m., it partly passed over at $200-210^{\circ}$, but evidently undergoes decomposition. It yields a crystalline slightly soluble sodium salt. A solution of this salt gives with copper sulphate a greenish precipitate, which seems to be a basic salt, and with silver nitrate a white precipitate, which becomes brownish on exposure to light, but does not blacken on boiling. Analyses were made of the acid (left in a vacuum till it ceased to lose weight) and of the crystallised sodium salt, with results corresponding to the formulæ $C_{10}H_{16}O_3$ and $C_{10}H_{15}NaO_3$.

This compound does not appear to be a ketonic acid, and the remarkable properties of its sodium salt lead to the suspicion, notwithstanding that it has not yet been crystallised, that it may be identical with Baeyer's nopic acid, a by-product recently obtained in the oxidation of crude pinene by permanganate (*Ber.*, xxix., 25). This, however, can only be settled by further inquiry, for which materials are already partly prepared.

*77. "An Apparatus for showing Experiments with Ozone." By G. S. NEWTH.

The special feature of this apparatus consists in the device for introducing reagents into the ozonised oxygen without disturbing the volume of the gas. The reagent is contained in a sealed capillary tube, which is retained in position by means of four small raised points of glass upon the walls of the inner and outer tubes of the ozone apparatus. The inner tube is ground to fit the outer one, and by a slight turn of the former the tube containing the reagent can be broken. In this way it is possible to show that the contraction in volume due to the absorption of ozone by turpentine is exactly twice as great as that which is produced by ozonising the oxygen, and also that when ozone is acted upon by potassium iodide a volume of oxygen equal to that of the ozone is liberated.

*78. "Note on Santalal and some of its Derivatives." By ALFRED C. CHAPMAN, F.I.C., and HERBERT E. BURGESS.

In connection with a study of certain hydrocarbons allied to the sesquiterpenes, upon which one of the authors is engaged, it became a matter of interest to determine more carefully the chemical properties of cedrene, and to compare it with the hydrocarbon obtained by the action of phosphorus pentoxide on santalal, with which it is generally said to be identical.

The cedrene was prepared by the fractional distillation of about 1 litre of cedar-wood oil under reduced pressure, and had a corrected boiling-point of $261-262^{\circ}$. Its density at $15^{\circ}/15^{\circ}$ was 0.9359, and it produced, in a 100 m.m. tube, a λ -rotation of 60° . Its refractive index for the red hydrogen line and for the sodium line was $\mu_H = 1.4991$; $\mu_D = 1.5015$.

Although cedrene is unsaturated, and combines readily with hydrogen chloride and bromine, no definite compounds with these substances could be isolated. Negative results were also obtained in the case of the oxides of nitrogen and nitrosyl chloride.

Santalal was next prepared by the fractional distillation of santal-wood oil. Its corrected boiling-point was found to be $301-306^{\circ}$, some decomposition occurring at this temperature. Its density was $d_{15^{\circ}/15^{\circ}} = 0.9793$; $d_{20^{\circ}/20^{\circ}} = 0.9761$, and its specific rotatory power at 27° was $-14^{\circ} 42'$ for sodium light.

Its refractive index for the lines C and D was $\mu_H = 1.5051$; $\mu_D = 1.5085$. Its specific refractive energy

is, therefore, 0.3039, and its molecular refractive energy 66.8. $C_{15}H_{24}O$ requires 66.3. Its general properties are those of an aldehyde.

On oxidation with an aqueous solution of potassium permanganate it yielded an acid crystallising from dilute alcohol in thin pearly plates melting at 76° . For this substance the name "santalenic acid" is suggested. This acid is still under investigation.

From santalal the hydrocarbon, $C_{15}H_{22}$, was prepared by treatment with phosphorus pentoxide and subsequent fractionation under reduced pressure. The main fraction was then obtained as a colourless liquid boiling between $140-145^{\circ}$ (25 m.m.). Its density at $15^{\circ}/15^{\circ}$ was 0.9359. In a 100 m.m. tube at 16° it produced a rotation of $5^{\circ} 45'$ to the right. This hydrocarbon is unsaturated, combining directly with hydrogen chloride and bromine, but no definite compound could be obtained. Attempts to prepare compounds with the oxides of nitrogen and nitrosyl chloride were equally unsuccessful.

So far as these results go they show that cedrene and the hydrocarbon from santalal are very similar, but not identical.

*79. "Second Note on the Liberation of Chlorine during the Heating of a Mixture of Potassic Chlorate and Manganic Peroxide." By HERBERT MCLEOD, F.R.S.

This paper is a reply to a criticism by O. Brunck (*Zeit. Anorg. Chem.*, 1895, x., 222) on a previous note, in which it was shown that chlorine is produced by heating a mixture of potassic chlorate and manganic peroxide. Brunck considers that the evidence is insufficient, and that the author was misled by the presence of potassic chloride mechanically carried over by the gas. Further experiments have been carried out in a different manner, arising from a suggestion of Dr. Armstrong. The mixture of potassic chlorate and manganic peroxide was heated in a test-tube by the vapour of boiling mercury, and the gas passed into an exhausted flask. After the lapse of some days, during which the suspended matter settled, the gas was pumped out through U-tubes containing solutions of sodic carbonate and potassic iodide. When the gas traversed the sodic carbonate first, no colouration was seen in the potassic iodide, even when this was done immediately after the gas was collected, showing the absence of ozone. On acidifying the sodic carbonate solution with nitric acid, and adding argentic nitrate, a precipitate of chloride was formed which was weighed, and from it the quantity of chlorine was calculated. In three experiments the quantities of chlorine were 0.064, 0.063, and 0.057 per cent on the quantity of potassic chlorate used. When the gas, after three days' rest, was passed through a solution of potassic iodide and then through sodic carbonate, the latter did not contain chloride, and the former solution was coloured; on determining the liberated iodine volumetrically it was found to correspond to a quantity of chlorine equal to 0.063 per cent on the chlorate. Sodic hydrate solution that was used for washing oxygen, prepared by heating the usual mixture, was found to contain permanganate, some oxides of manganese having been mechanically carried into the solution, showing that the gas contained chlorine, for ozone does not produce permanganate when in contact with sodic hydrate containing manganic peroxide.

*80. "Polymorphism as an Explanation of the Thermochemical Peculiarities of Chloral and Bromal Hydrates." By WILLIAM JACKSON POPE.

Berthelot has observed that the heat of combustion of chloral hydrate decreases as the time elapsing since fusion and solidification of the sample increases; the same observation has been made by Bruner respecting bromal hydrate. No explanation of this peculiarity is offered by either of these chemists, although Bruner states that other substances such as thymol and menthol, which are pasty after solidification, do not show the same behaviour.

In the case of chloral hydrate at least, the explanation

of the gradually decreasing heat of combustion is a purely crystallographic one. On cautiously melting the hydrate on a microscopic slide under a cover slip, and allowing the slide to cool, solidification readily occurs, and a thin crystalline film of the substance suitable for micro-crystallographic examination is obtained; it consists entirely of felted acicular crystals, most of which are so orientated that the optic axial direction of an optically negative uniaxial substance is perpendicular to the surface of the slide; in other crystals the optic axis emerges obliquely, and sometimes the crystals are slightly biaxial. A few of the needles may be truly biaxial, but this can hardly be stated definitely. After several hours at the ordinary temperature, minute rhomboidal plates make their appearance amongst the needles, and, after twenty-four hours, have become sufficiently large for crystallographic examination. The number and size of these plates, which belong apparently to the monosymmetric system, increase continuously, whilst the number of needles decreases until, after six or eight days, none but the monosymmetric plates remain. It is thus evident that on solidification of chloral hydrate a uniaxial form is obtained which very slowly changes into a biaxial modification stable at ordinary temperatures; this change must be accompanied by an evolution of heat, as are all changes of the kind, so that freshly solidified chloral hydrate has a larger heat of combustion than a sample solidified several days before burning. The change of any particular spot in the slide may be best observed and recorded photographically, and several good series of micro-photographs have been taken between crossed Nicols at definite intervals of time, which show the transition in a very perfect manner.

On similarly examining bromal hydrate, no very distinct evidence of change is obtained, the solidified mass being scarcely suitable for micro-crystallographic examination. The photographic record, however, seems to indicate a change of some kind in the plate.

The thermo-chemical behaviour of thymol must, as found by Bruner, be quite normal, because no crystalline change of any kind occurs in it after solidification has once occurred.

After melting menthol, the other instance quoted by Bruner, it solidifies from centres giving a radially crystallised film. There is usually just time to give a photographic plate an exposure of three minutes on the preparation, however, before a change of crystalline form sets in and the menthol becomes rapidly converted into a mass of very minute crystals which show aggregate polarisation; after this no further change occurs. Since the time elapsing between cooling and the formation of the crystalline modification of menthol stable at ordinary temperatures is too short to allow of the substance being weighed and introduced into the calorimetric bomb, the heat of combustion determined has always been that of the modification stable at ordinary temperatures.

The crystallographic examination of these substances shows that thermo-chemical data respecting solid organic substances should always be accompanied by a crystallographic description of the material used.

81. "*Explosion and Detection of Acetylene in Air.*" By FRANK CLOWES, D.Sc.

The behaviour of mixtures of air with gradually increased proportions of acetylene, when brought into contact with flame, were studied by a method recently described by the author.

The method enables mixtures in varied and accurately known proportion to be rapidly prepared. The proportion of acetylene was progressively increased from 1 to 82 per cent.

The mixture containing 3 per cent of acetylene was the first which was affected by contact with the flame placed either above or below. A pale green flame slowly traversed the mixture, showing that it was feebly explosive. As the proportion of acetylene was increased, the

rapidity of combustion increased, and even a small volume of the mixture gave decidedly explosive effect.

When 22 per cent of acetylene was present, the explosive combustion of the mixture was attended with a slight separation of unburnt carbon. As the proportion of acetylene was increased, the separation of carbon was more marked. The limit of explosibility, as judged by the flame traversing the mixture, was reached when 81 per cent of acetylene was present.

The range of explosibility of mixtures of air with acetylene, extending from 3 per cent of acetylene to 81 per cent, is extraordinarily wide, exceeding that of any combustible gas yet experimented with. It seems highly probable that the appearance of combustion extending through the mixture with the higher proportions of acetylene is partly due to acetylene being an endothermic compound. Accordingly, the combustion of a small portion of the acetylene in contact with the kindling flame, starts the decomposition of the remainder of the acetylene, with the production of heat and the appearance of combustion. This probably explains why air containing much acetylene becomes heated throughout, when it is kindled at one point, and thus extends the range of explosibility of mixtures of acetylene with air.

In estimating the percentage of acetylene in air, if the amount does not reach the lower explosive limit of 3 per cent, the most convenient method was the passage of the air over a standard hydrogen flame, and an examination and measurement of the halo or "flame-cap" which was seen in a darkened room over the hydrogen flame. A laboratory apparatus suitable for this purpose is nearly perfected, and will probably be found convenient as a means for measuring accurately the percentage of any combustible gas present in air. About 600 c.c. of the mixture are required for the estimation, which is completed in a few seconds.

When air containing less than 3 per cent of acetylene was passed over the standard 10 m.m. hydrogen flame, the flame at once became yellowish green in tint. A halo or "cap" was at the same time seen, the height of which increased so rapidly with the increase in the percentage of acetylene, that the last estimation was made by the use of a reduced 5 m.m. hydrogen flame. The measurements of the "cap" over the 10 m.m. hydrogen flame were as follows:—0.25 per cent, 17 m.m. cap; 0.5 per cent, 19 m.m.; 1 per cent, 28 m.m.; 2 per cent, 48 m.m. Over the 5 m.m. flame, 2.5 per cent gave 56 m.m. cap, and 2.75 per cent 79 m.m. cap. When the percentage reached 3 per cent it burnt throughout, giving no cap.

82. "*On the Occurrence of Quercetin in the Outer Skins of the Bulb of the Onion (Allium Cepa).*" By A. G. PERKIN and J. J. HUMMEL.

Zeuch (*Farben und Farbenkunde*, 1825, i., 434) has described the dyeing properties of these skins. The colouring matter was obtained by the authors in the form of glistening yellow needles of the formula $C_{15}H_{10}O_7$, which yielded compounds with mineral acids, the sulphuric acid compound $C_{15}H_{10}O_7 \cdot H_2SO_4$ was analysed. On acetylation, a compound, $C_{15}H_5O_7 \cdot (C_2H_3O)_5$, forming colourless needles, melting-point $190-191^\circ$, was obtained, and by decomposition with fused alkali, phloroglucin and protocatechuic acid formed the principal products. With mordants it dyed shades similar to those given by quercetin, the colouring matter of quercitron bark, and was thus proved to be identical with this substance.

Comparative dyeing experiments showed that the colouring matter of onion skins was quite equal to that of such well-known dye-stuffs as old fustic and quercitron bark.

(To be continued.)

Exhibitionism.—We regret to learn that Queensland is preparing to hold an "International" Exhibition. Had it been purely Imperial it would have had our best wishes.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxixiii., No. 5, August 3, 1896.

Study of the Diamantiferous Sands of Brazil.—Henri Moissan.—Thanks to the kindness of Professor Lacroix, of the Museum of Natural History, we have been able to examine if the diamantiferous sands of Brazil contain also microscopic diamonds. 4500 grms. of the sand were sifted and yielded 1350 grms. of a powder consisting almost entirely of silica. The attack is very tedious, and it is only after a dozen alternate treatments with hydrofluoric acid and boiling sulphuric acid that we arrived at a residue of 2 grms. The substance is then treated with melting fluopotassium hydrofluoride, and is then attacked with potassium bisulphate, when we obtained a residue of 2 grms. This residue contains portions consisting of small transparent grains, some spangles of native gold and platinum, and of small black brilliant crystals having the aspect of graphite. We separated some of the latter and transformed them into graphitic oxide, which on deflagration yielded pyrographitic oxide. After having characterised the graphite all the residue was treated with methylene iodide. The portion more dense than this liquid was treated anew with fluoride hydrofluoride and then with bisulphate. An attack with aqua regia caused the precious metals to disappear. We have then been able to separate some black fragments and transparent fragments which had no action upon polarised light and which burnt completely in oxygen, yielding a white precipitate with baryta water. This residue contains brilliant grains acting upon polarised light, having an elongated form, a corroded surface, and which have been ultimately caused to disappear by successive attacks. This Brazilian diamond contains black diamonds of a shagreened surface, also transparent diamonds of irregular form, and lastly graphite. There exist, therefore, in nature, both at the Cape and in Brazil, microscopic diamonds, black or transparent, and in both cases accompanied with graphite.

Oxidation of the Organic Matter of the Soil.—P. P. Dehérain and E. Demoussy.—Although it is at temperatures exceeding 100° the oxygen of the air burns rapidly the organic matter of the soil, oxidation is fairly active between 40° and 60°; we can thus understand how in hot regions lands ploughed but left without manure become barren by the disappearance of the humus, which the spontaneous vegetation had accumulated. In our cool regions this disappearance is slower; still the fields of the experimental farm of Grignon, bearing various crops and left without manure, lose in ten years the half of their organic matter. If the soil is plentifully manured the oxidation is, in our opinion, too slow, whence the incessant work which farmers have to undertake to allow the oxygen to penetrate into the soil and to bring the humus into such a state that nitrification can be effected.

Biological Chemistry and Mechanics.—A. Chauveau deals with the following subjects:—What we must think of the alleged sterile dissipation of energy in the execution of muscular work. Extension of the Applications of the law of energetic equivalence in biology. Not adapted for insertion.

Non-Refraction of the X Rays by Potassium.—F. Beaulard.—One of the most important characters of the X rays is that they are not refracted, or at least that they do not undergo any refraction perceptible and capable of easy measurement with our present appliances. The very precise researches of M. Gouy (*Comptes Rendus*, May 26th and July 6th) have shown that aluminium does not refract

the X rays and that the refraction, if it exists, is insensible.

$$(n - 1 < \frac{1}{10^6})$$

The author has attempted to refract the X rays through a prism of potassium. The result was negative; the deviation, if existing, is less than 10"; the index therefore differs from unity by a quantity inferior to 1/10,000th.

Nitrogen and Argon in Fire-damp and in the Gas of Rochebelle.—Th. Schloesing, jun.—(See p. 87).

Specific Heat of Sulphur in the State of Viscosity.—J. Dussy.—The specific value of viscous sulphur is distinctly higher than it presents in the liquid state. The curve which represents $2 \frac{T}{0}$ (the total heat lost by 1 grm.

of sulphur in passing from T to 0°) seems to experience a change of pace about 230°. The author hopes to extend the same study to selenium. Sulphur, if tempered at heats comprised in an interval between 157° and 175°, solidifies very rapidly, taking a characteristic vitreous aspect, which does not seem to have been as yet pointed out. Thus sulphur cast at 165° solidifies in filaments, with a distinctly vitreous fracture; a mass of sulphur at 220°, thrown at once into cold water and then left to itself, presents after solidification an external layer of soft sulphur, then a vitreous layer, and finally a layer of prismatic sulphur. We generally approximate soft sulphur to vitreous selenium. The existence of vitreous sulphur legitimates this approximation more completely.

Contributions to the Study of the Analytical Characters of the Compounds of Tungsten.—E. Defacqz. (See p. 88).

Action of Aluminium Chloride upon Benzene containing Thiophene.—Eyvind Baedker.—If we heat crystallisable benzene with aluminium chloride on the water-bath we observe at a low temperature the formation of hydrogen sulphide and hydrochloric acid, and if we collect the vapours given off in a solution of lead acetate, lead sulphide is precipitated.

On New Mixed Trimethylenic Compounds.—Louis Henry.—The compounds obtained are trimethylene chloriodide, $\text{ClCH}_2\text{—CH}_2\text{—CH}_2\text{I}$, and trimethylene nitrochloride, $\text{ClCH}_2\text{—CH}_2\text{—CH}_2\text{(NO}_2\text{)}$.

Rapid Determination of the Components of a Mixture of Primary, Secondary, and Tertiary Amines having the same Aliphatic Radicle.—Ch. Gassmann.

MISCELLANEOUS.

Various Methods of Formation of Blue Nitrodisulphonic Acid and of its Salts.—Paul Sabatier.—As the author has previously shown, we can obtain the blue acid by causing a regulated mixture of nitric oxide and of air to react upon sulphuric acid saturated with sulphurous anhydride. But it may also be obtained by the reduction of the nitrosulphuric liquid, by the action of sulphurous acid upon nitrosulphuric liquid, and by the action of nitric oxide upon a metallic sulphate in a sulphuric solution.—*Comptes Rendus*, cxixiii., No. 4.

Behaviour of Gold in Pyrites during Weathering.—W. Mietzchke.—Auriferous pyrites, whether in solid rock or in a loose condition, display the peculiar behaviour that the gold uniformly distributed in the mass in the state of sulphide, in proportion as it is converted into an oxidised product, moves towards the middle of the mass. Hence the pyritic nucleus of a half-weathered crystal shows double the proportion of gold than does the average mineral before decomposition. In a fully weathered specimen the author found a granule of gold with crystalline surfaces. The confirmatory specimens were obtained from the Orenburg Government (Russia).—*Berg. u. Hütten. Ztg. and Chem. Zeitung*.

A Filter of Cellulose.—Henri Pottevin.—With fibres of cellulose, finely pulverised and sifted, and suspended in water, we obtain a paste which, if allowed to dry slowly, gives plates which in the thickness of a few m.m. are capable of serving as a substitute for porcelain. These plates, for filtration, must be kept between two layers of stoneware or of perforated metal. Filtration through such plates, arranged like a filter-press, was found to sterilise water.—*Comptes Rendus*, cxxiii. No. 4.

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1918.

ACTION OF HYDROGEN SULPHIDE ON CUPRIC SALT SOLUTIONS.

By BOHUSLAV BRAUNER, Ph.D., F.C.S.,
late Berkeley Fellow of Owens College.

MR. COPPOCK'S paper in one of your recent issues (CHEM. NEWS, vol. lxxiii., p. 262) induces me to give a short account of my experience on the above subject.

The fact that the black precipitate obtained from cupric solutions by the action of hydrogen sulphide is Cu_4S_3 , and not CuS , is not due to Menshutkin, but—as the author seems to be unaware—to Julius Thomsen, who, in 1878, published a short paper on that subject (*Berichte*, xi., p. 2043).

Several years ago I undertook, with Mr. A. Polan, a work on the above subject which gave only experimentally, but not theoretically, definite results, and which were never published; Mr. Polan having left the University meanwhile. The facts arrived at are the following:—

It was proved, first, that the said "black," but better, greenish black or dark olive-green, precipitate which is formed by the action of hydrogen sulphide in excess on a solution of a cupric salt and removing the excess of the gas by a current of carbon dioxide, really contains copper and sulphur in the exact atomic proportion $\text{Cu} : \text{S} = 1 : 1$; all the sulphur being, however, not combined to copper, but existing partly in the free state. But whereas in Thomsen's experiments cupric sulphate was precipitated with an excess of sodium sulphide—which dissolved the excess of free sulphur, forming a polysulphide—a different method was employed in our experiments.

Solutions of cupric sulphate or chloride in water:—(1) More or less dilute; (2) more or less acidified; and (3) either cold or at a higher temperature, were precipitated with (4) a slow or a rapid current of hydrogen sulphide in excess, i.e., completely.

In order to avoid a possible oxidation of the precipitate in the air, it was filtered, washed first with aqueous hydrogen sulphide, then in an atmosphere of carbon dioxide with water free from air, then with alcohol, repeatedly with distilled carbon disulphide, until all free sulphur was removed; again with alcohol, in order to remove any trace of carbon disulphide; and finally with ether, keeping the precipitate all the time in an atmosphere of carbon dioxide.

The completely washed and dried finely-divided precipitate undergoes an oxidation in the air, but this circumstance was quite immaterial in regard to the course of analysis used for ascertaining the composition of the dark olive-green powder obtained.

An unweighed quantity of the sulphide was brought into a wide-necked bottle; it was then moistened with water, some potassium chlorate was added, and a short test-tube containing fuming nitric acid was inserted, after which the bottle was closed with a moistened and well ground glass stopper, which was fastened with a cloth and string. By inclining the bottle, small quantities of nitric acid are poured out successively from the short test-tube (which possesses a small hole near its upper end, so that it is easily put in and out with a hooked platinum wire) upon the wet mixture of the copper sulphide with potassium chlorate (on using dry mixtures of some sulphides explosions take place). When every reaction in the cold has ceased, the bottle is opened and the oxidation completed at a moderate heat.

After removing all nitric acid by evaporation, finally with hydrochloric acid, the clear solution was brought to

a definite volume, and two or more aliquot equal portions were measured out.

One part was used for the determination of copper, the other for the determination of sulphur, and from the relations of copper to sulphur the composition of the precipitate remaining after the above treatment was calculated under the plausible assumption that the precipitate contains only copper and combined sulphur, any free sulphur having been removed by the above process.

The results obtained may be shortly summed up as follows:—

1. The original precipitate, unwashed with CS_2 , &c., always consists of copper, combined sulphur, and free sulphur.

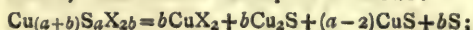
2. The precipitate washed with CS_2 , &c., never contains copper and sulphur in the atomic proportion CuS .

3. This precipitate contains copper and sulphur in very varying proportions expressed by the general formula $\text{Cu}_n\text{S}_{(n-x)}$, in which always $x < \frac{1}{2}n$, i.e., its composition lies between that of CuS and Cu_2S ; it, therefore, does not always consist of Thomsen's Cu_4S_3 .

4. It is interesting to find that the composition of the precipitate may be represented dualistically, as if it consisted of a mixture or compound of cupric sulphide with cuprous sulphide in definite proportions; the relative number of molecules being expressed by small integers. Further research must show whether this is not due to chance only. Such cases are, e.g., $5\text{CuS} + 2\text{Cu}_2\text{S}$, $3\text{CuS} + \text{Cu}_2\text{S}$, $2\text{CuS} + \text{Cu}_2\text{S}$, &c.

From the detailed study of the action of hydrogen sulphide upon solutions of arsenic and antimony acids, as undertaken by Brauner and Tomicèk, Le Roy McCay, Brauner and Bosèk, it results that, as long as hydrogen sulphide is not present in excess, oxysulpho-compounds (sulphoxy-acids) of arsenic and antimony are formed, which, by the further action of hydrogen sulphide, owing to the formation of oxygen and sulphur compounds of the higher form RX_5 and the lower form RX_3 , yield a mixture of the pentasulphide with the trisulphide.

In regard to the fact that—(1) In copper (and also nickel) is left a part of the property of forming soluble double sulphides (sulpho-salts), in which respect it approaches the more negative elements of the analytical arsenic-antimony group (Ge, Sn, As, Sb, Mo, Te, W, Pt, and Ir); and (2) that hydrogen or other sulphides when acting upon an excess of a cupric solution give rise to the formation of black or brown solutions, containing copper probably in a similar state in which antimony is contained in a mixture of an excess of antimonious acid solution with hydrogen sulphide; it may be concluded, by analogy, that in the first phases of the reaction compounds of the general formula $\text{Cu}_{(a+b)}\text{S}_a\text{X}_{2b}$ (where $\text{X} = \text{Cl}, \frac{1}{2}\text{SO}_4$, &c.) are formed, which further decompose as follows:—



so that by a further action of hydrogen sulphide a mixture of cupric sulphide with cuprous sulphide results.

The experiments hitherto made have not yet yielded a sufficient material from which might be concluded whether the reaction is going in one direction (production of more CuS) or the other (Cu_2S), as the temperature is lower or higher, the current of hydrogen sulphide more or less rapid, and the quantity of acid present larger or smaller. This may be shown by further experiments, without, as I hope, trespassing on Mr. Coppock's ground of research.

Chemical Laboratory,
Bohemian University, Prague.

Examination for free Hydrochloric Acid in the Gastric Liquid.—J. Sjögnist (*Scandin. Archiv. Physiol.*).—The author recommends a procedure which consists essentially in precipitating the dissolved baryta as chromate, and determining the chromic acid liberated by an acid by Zulkowsky's iodometric process.

STUDY ON THE NITROGEN AND THE ARGON
OF FIRE-DAMP.

By TH. SCHLÆSING, Jun.

I HAVE the honour of presenting to the Academy a continuation of my researches on the composition of fire-damp. I have been led to study this gas as a product of the slow decomposition of vegetable matter in the particular case of its transformation into coal. I have at first attended to its combustible part; but soon the incombustible portion, or, more strictly speaking, the nitrogen and the argon of this portion, have seemed to me also of interest.

There is always nitrogen in fire-damp. Its proportion varies within very wide limits. In twenty-three specimens from different localities I have obtained as extreme ranges 0.75 and 30 per cent. Whence comes this nitrogen? It is, I think, most commonly admitted that it has been disengaged by nitrogenous constituents of vegetable matters which have passed into the state of coal. It seems very difficult to admit such an origin, for in slow decompositions reproduced in the laboratory we neither observe such a variability, nor, above all, such an exaggeration in the proportion of the nitrogen set at liberty. It was therefore natural to suspect the air as the possible source of the nitrogen of fire-damp. I examined if argon was present in this nitrogen, and I found 1.1 per cent—a proportion very near that (1.19) which characterises the nitrogen of the atmosphere. This seemed evidence in favour of the atmospheric origin of the nitrogen of fire-damp.

M. Leproux was aware of these results. To permit me to verify them, he offered me fire-damp from St. Etienne and Plat-de-Gier, which he knew was disengaged under a great pressure, and which, consequently, was derived from portions of the rock into which the air could not have penetrated in recent times. If the nitrogen of such fire-damp possessed the proportion of argon peculiar to atmospheric nitrogen, we might admit that the air to which it belonged had been imprisoned in the coal at the remote epoch when the fire-damp was formed; that is to say, according to the expression of M. Leproux we were in presence of *fossil air*.

Thus it became more and more interesting to determine exactly the proportion of argon contained in the nitrogen of fire-damp.

A first determination made on the fire-damp of Saint Etienne gave 1.18 argon per cent of nitrogen. This was exactly the same proportion as in atmospheric nitrogen. With a recommendation from M. Aquillon, the Inspector-General of Mines, I obtained fire-damp from various mining companies, taken as far as possible from blow-holes which yielded the gas at a considerable pressure.

Each specimen was collected by passing into series of four or six bottles, each of 6½ litres, a current of fire-damp which drove out the air by displacement. The bottles were then closed by means of good pinchcocks acting on good caoutchouc tubes. Collecting fire-damp over water must be avoided if we wish to reach great accuracy; for the water, which dissolves nitrogen and argon decidedly, but unequally, might alter the proportion of the two gases sought for, diminishing or increasing it, according to the cases.

To arrive at the proportion in question, it is necessary at first to separate the nitrogen along with its argon. To this end the fire-damp is passed over copper oxide heated to redness and then into potassa. For this operation I find it very advantageous to use an apparatus analogous to that which I have used for the determination of argon, in which a mercurial pump causes the gases to circulate constantly over the reagents. We introduce the fire-damp into the apparatus gradually, as it disappears until we have obtained a sufficient volume of nitrogen. A vacuum is made at the outset to eliminate the air, and again at the end to extract the nitrogen and

bring it into a tube, where it is measured. Of this nitrogen we take a small specimen and determine its degree of purity eudiometrically. We generally find that it contains from 0 to 0.5 per cent of carbonic acid and of combustible gas, of which we take account in the calculations. We finally determine the argon thus prepared according to a process which I have already described. I have spoken of argon to simplify the description; but the true nature of the element determined is not absolutely established by the operations described. A spectral determination is required. I have made such a determination, making use of Plücker tubes, into which I introduced the gaseous residues in question with all the precautions requisite.

I cannot bring forward to-day all my results and my conclusions. I can merely say that in the nitrogen extracted from fire-damp I have always found a notable proportion of argon. But there follows a question to which an answer is required—Does the argon of fire-damp come from coal?

I have sought for argon in the coals of St. Etienne and of Plat-de-Gier.

The specimens analysed have been finely pulverised, then submitted to a vacuum and to a true determination of nitrogen of volume. The gas obtained was measured, verified as to its purity by eudiometric analysis, treated so as to isolate the argon: 22 grms. of coal (not dried) from St. Etienne yielded 243 c.c. or 3.304 grms. of nitrogen (say, by weight 1.38 per cent), which, after the operations required for separating the argon, left a gaseous residue of about 0.08 c.c. In like manner, with 18.3 grms. of the coal of Plat-de-Gier, I have obtained 196 c.c. or 0.245 gm. nitrogen (say, 1.34 per cent), whence there was extracted a residue of about 0.05 c.c. These residues are about equivalent to the argon which the atmospheric nitrogen might have furnished. They might further represent the foreign impurities in the substances analysed derived especially from the solutions of potassa, which had to be used in very important quantities.

In fine, the coals examined contained at most, if any, 1/200,000th of an element comparable to argon. It cannot, therefore, be thought that problematical traces of this element can exert an influence on the composition of the fire-damp.—*Comptes Rendus*, cxxiii., p. 233.

ASSAY OF GOLD ORES AND SANDS BY
AMALGAMATION AND WITH THE BLOWPIPE.

By HAMILTON MERRIT.

The author takes 1 kilo. of the material, passes it through a sieve of 60 meshes per square inch, and adds 1 oz. (31 grms.) of mercury and sodium amalgam. The latter prevents the excessive scattering of the mercury in the pan during amalgamation. The admixture of the mercury and ore is effected with a wooden pestle and is continued for an hour. The results obtained correspond approximately with those of amalgamation in the mill. Every grain of gold weighed represents 2 ozs. per ton. For decomposing the amalgam he uses, instead of a retort, sheet-iron moulded into the shape of a cup. The concentrates obtained are tested with the blowpipe quantitatively to ascertain if gold is still present. For a quantitative determination the grains are measured with Plattner's scale. In this manner ores may be used which contain not more than 60 marks of fine gold per ton.—*Inst. Amer. Mining Engineers*, Pittsburg Meeting, Feb., 1896, and *Chemiker Zeitung*.

The Thalleioquin Reaction. — A. Belahoubek and Sedlecky (*Pharm. Post*).—The authors show that this reaction is interfered with by the presence of caffeine or antipyrin.

AN
EMPIRICAL RELATION BETWEEN MELTING-
POINT AND CRITICAL TEMPERATURE.

By F. W. CLARKE.

ALTHOUGH many papers have been written upon relations between boiling-point and critical temperature, the melting-points of substances, at least in this connection, seem to have been little considered. And yet a glance at the subject will indicate its importance. For any substance the limits of the solid state are the absolute zero and the melting-point; while the extreme limits of the liquid condition are the melting-point and the critical temperature. A comparison of these values, therefore, will give for each substance the relative thermometric lengths of the two states of matter, and the results obtained, although empirical, have very decided interest. Unfortunately many of the compounds of which the critical temperature is known, have never had their melting-points determined, and hence the available data are very meagre.

Representing the ordinary melting-points by t and the critical temperatures by T , the relation between them, on the absolute scale, is best represented by the formula—

$$\frac{T + 273}{t + 273} = 2$$

For the following substances this ratio is very nearly = 2; the data, except when otherwise stated, being taken from Landolt and Börnstein's tables. Fractions of degrees less than 0.5 are neglected.

	t . Degrees.	T . Degrees.	Ratio.
Nitrogen	-214.0	-146.0	2.18
Carbonic oxide ..	-207.0	-139.5	2.02
Argon (Olszewski) ..	-190.0	-121.0	1.83
Methane	-186.0	-82.0	2.19
Hydrochloric acid ..	-112.5	+52.0	2.02
Hydrogen sulphide ..	-86.0	+100.0	2.00
Ammonia	-75.0	+130.0	2.03
Benzene	+3.0	+288.5	2.04
Acetic acid	+17.5	+322.0	2.05

In other words, for these nine substances the absolute melting-point is very nearly, if not exactly, one-half the absolute critical temperature, and the thermometric lengths of the solid and liquid states are approximately equal. Assuming the errors of observation to be evenly distributed in each case between the two temperature factors, we may average the latter and so compare the mean values with those actually recorded. The results are as follows:—

	Found.		Average.	
	t . Degrees.	T . Degrees.	t . Degrees.	T . Degrees.
N ₂	-214.0	-146.0	-211.0	-149.0
CO	-207.0	-139.5	-206.5	-140.0
A	-190.0	-221.0	-195.0	-117.0
CH ₄	-186.0	-82.0	-180.0	-87.0
HCl	-112.5	+52.0	-111.0	+51.0
H ₂ S	-86.0	+100.0	-85.5	+100.5
NH ₃	-75.0	+130.0	-73.0	+128.0
C ₆ H ₆	+3.0	+288.5	+4.0	+287.0
C ₂ H ₄ O ₂ ..	+17.5	+322.0	+22.0	+317.9

When we consider the uncertainty of some of the measurements, the agreement is certainly very close.

This simple relation, however, is not general. In all, I have examined the data for about thirty substances, and no universal rule appears. There are, nevertheless, other regularities apparent which connect certain allied substances with one another, and two such groups I subjoin:—

	t . Degrees.	T . Degrees.	Ratio.
C ₂ N ₂	-34.5	+124.0	1.67
N ₂ O ₄	-10.0	+171.0	1.64
NO	-167.0	-93.5	1.70
N ₂ O	-99.0	+35.5	1.77

These compounds run closely together, and are alike in being gaseous compounds of nitrogen. The next group contains five aromatic bodies.

	t . Degrees.	T . Degrees.	Ratio.
<i>o</i> -Xylene	-45.0*	+358.0†	2.77
<i>m</i> -Xylene	-53.0	+346.0†	2.81
C ₆ H ₅ Cl	-40.0	+361.0	2.78
C ₆ H ₅ Br	-30.5*	+397.0†	2.75
C ₆ H ₅ I	-28.5*	+448.0†	2.94

* v. Schneider. † Altschul. ‡ Young; theoretically determined.

Here, again, there is an essential identity of ratio with related constitution—a fact which suggests that the method of discussion applied to larger masses of data is likely to give information of considerable theoretical value.

For most of the other substances which I have considered, the ratio ranges between 2.2 and 3.0. For carbon dioxide its value is only 1.41; for ether it is 3.06. In the latter case the thermometric lengths of the solid and liquid states, therefore, are as one to two. A few bodies only give ratios higher than three. These are—besides ether—

CS ₂	3.36
PCl ₃	3.47
Alcohol	3.59

Other values are—

Br ₂	2.17	H ₂ O	2.34
Cl ₂	2.44	SnCl ₄	2.47
SO ₂	2.22	CHCl ₃	2.62
CCl ₄	2.25	C ₂ H ₄	2.75

Paraxylene gives the ratio 2.14, varying widely from its isomers.

Concerning the quantity of heat necessary to raise a body from absolute zero to the melting-point, and then from the melting-point to the critical temperature, the data are altogether wanting; but the ratio between those two quantities would certainly be significant. For the regularities which I have here pointed out I have no theoretical explanation to offer. If, however, they serve to stimulate the determination of other low temperature melting-points for compounds of which the critical temperatures are known, this paper will have served a useful purpose. The relations which are already apparent cannot be meaningless, and others must be discoverable.—*American Chemical Journal*, xviii., No. 7, July, 1896.

THE INTRODUCTION OF STANDARD METHODS
OF ANALYSIS.*

By the Baron HANNS JÜPTNER von JONSTORFF
(Neuberg, Austria).

(Continued from p. 83).

δ. *Not taking into consideration Volume Correction.*—The errors due to this in the measurement of gases are so great that in the case of gases the correction ought never to be overlooked. But even in the case of standard solution, overlooking this question of the volume correction may lead to unpleasant errors, as, for instance, is shown by the accompanying table drawn up by A. Schulze (Fresenius, *Zeit. f. Anal. Chemie*, 1882, p. 167):—

* Read before the Iron and Steel Institute.

Temp. Degr. C.	Normal.							Temp. Degr. C.
	Oxalic Acid.	Hydro- chloric Acid.	Nitric Acid.	Sulphuric Acid.	Sodium Carbonate.	Caustic Soda.	Water in Glass.	
5	+0.0018	+0.0017	+0.0026	+0.0025	+0.0026	+0.0028	+0.0009	5
6	17	16	25	24	25	26	9	6
7	16	15	23	22	23	24	9	7
8	15	14	21	21	21	22	9	8
9	14	13	19	19	19	20	8	9
10	13	12	17	17	17	18	8	10
11	12	11	15	15	15	16	7	11
12	10	9	13	13	13	14	7	12
13	8	8	11	11	11	11	6	13
14	7	6	9	9	9	9	5	14
15	5	5	6	6	6	6	3	15
16	3	3	4	4	4	4	2	16
17	1	1	1	1	1	1	1	17
17.5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	17.5
18	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	18
19	3	3	4	4	4	4	2	19
20	6	5	7	7	7	7	4	20
21	8	7	10	10	9	10	6	21
22	10	9	12	12	12	13	8	22
23	13	12	15	15	15	16	10	23
24	16	14	18	18	18	19	12	24

This table, which relates to the normal solutions mentioned at the temperature of 17.5° C., gives the correction for one cubic centimetre of the solution. The correction is therefore made by adding the product of the number of cubic centimetres used with the factor given in the table—observing whether it is a — or + quantity—to the number of cubic centimetres of the standard solution added in the course of the determination. Supposing, for instance, a titration had been made at a temperature of 12° C., and that 21 c.c. of normal sulphuric acid had been used, then $21 + 21 \times 0.0013 = 21.0273$ c.c. is the correct quantity of 17.5° C. If, on the other hand, 21 c.c. at the temperature of 24° C. was necessary, then $21 - 21 \times 0.0018 = 21 - 0.0378 = 20.9622$ c.c. of acid at a temperature of 17.5° C. If, again, a titration with normal sulphuric acid were effected once at a temperature of 12° C. and again at 24° C., and 19.974 c.c. were used in the one case and 20.036 c.c. in the other (both of which exactly represent 20 c.c. normal sulphuric acid at 17.5° C.), and no correction had been made for the temperature, the two determinations would then show a difference of—

$$\frac{100(20.036 - 19.974)}{19.974} = 0.31 \text{ per cent.}$$

2. *Errors which may be caused by the Adhesion of the Liquids to the sides of the containing Glass Vessels.*—These must be taken into consideration, both in the marking and in the use of the measuring vessels. Measuring flasks, for instance, must be marked for their actual contents, burettes and pipettes, however, for the solution as run out; that is to say, in such a way that the solution as run out shall correspond with the value shown by the division. Some of the solution will still remain, however, attached to the glass sides, the quantity being dependent on the degree of fluidity and adhesion of the liquid. This, with adequate time allowed, drains together again, so that, when titrating, one should wait about two minutes between every reading. In the case of pipettes, the quantity of solution that flows out is most constant when the point of the pipette is placed in contact with the side of the vessel, and subsequently wiped off on it.

Temp. of the pipette and of the normal solution.	Plus or Minus quantity in thou- sandths which flowed from the pipette.		Quantity in thousandths, according to the difference in the expansion of the normal solution and of glass.	Gay- Lussac corr.
	I.	II.		
5° C.	+0.55	+0.57	+0.723	+0.1
10°	+0.40	+0.44	+0.500	+0.2
15°	0	0	0	0
20°	-0.70	-0.72	-0.750	-0.6
25°	-1.74	-1.75	-1.775	-1.6

In addition to these sources of error, the temperature also influences the quantity of solution that will flow out, as is shown by the accompanying short table given by Mulder (*Die Silberprobirmethode*).

(To be continued).

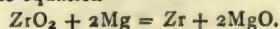
ZIRCONIUM TETRAIODIDE.

By L. M. DENNIS and A. E. SPENCER.

With the exception of the tetraiodide all of the normal halides of zirconium have been prepared and described, the fluoride, chloride, and bromide being white, crystalline, sublimable solids.

A few attempts to make the iodide are recorded in the journals, but in no case was the normal compound, zirconium tetraiodide, ZrI_4 , obtained. Melliss (*Zeitsch. Chem.*, 1870, 296; *Fsb.*, 1870, 328) passed the vapour of iodine over a glowing mixture of zirconia and carbon; he also treated zirconium tetrabromide with potassium iodide, but in neither case did zirconium tetrachloride result. Hinsberg (*Ann. Chem.*, Liebig, cccxxxix., 253) added an aqueous solution of barium iodide to a solution of zirconium sulphate, filtered off the barium sulphate, and evaporated the filtrate over concentrated sulphuric acid. He obtained a compound of the formula $Zr_2I_3O_3$, or $ZrI(OH)_3$. He also passed the vapour of iodine over a heated mixture of zirconium dioxide and carbon, and states that no reaction whatever took place. Bailey (*CHEM. NEWS*, lx., 8) states that "zirconium* is acted upon by chlorine and bromine, in which, on gentle heating, it undergoes vivid combustion, forming the tetrahaloid derivatives, and this is, indeed, a convenient method for obtaining these bodies. The iodide could not be obtained."

In the work here to be described the authors first attempted to prepare zirconium tetraiodide by passing the vapour of iodine over heated zirconium. The zirconium first used was made by reducing zirconium dioxide with magnesium powder, the two substances being mixed in the proportion employed by Winkler (*Ber. d. Chem. Ges.*, xxiii., 2664; xxiv., 888) and demanded by the equation—



This mixture was heated in hydrogen in the usual manner, and the resulting black powder was removed from the boat, thoroughly ground, and again heated in

* Prepared by the reduction of zirconia with magnesium powder.

hydrogen to insure complete reduction. To free it from magnesia, the product was treated with a saturated solution of ammonium chloride. During this treatment a gas of very disagreeable odour was evolved. It is doubtless similar to that observed by Winkler at this point. The powder was then warmed with dilute 12 per cent hydrochloric acid, and, after collecting it on a filter, it was washed with water containing hydrochloric acid, then with alcohol and ether, and finally was dried in a current of hydrogen. The analysis gave—

	Per cent.
Zirconium	80.670
Silicon	0.807
Magnesium	0.117
Hydrogen	0.362
Oxygen (diff.)	18.044
	100.000

These results agree quite closely with those obtained by Winkler (*Ber. d. Chem. Ges.*, xxiii., 2667), and indicate that the product of the reduction is chiefly zirconium monoxide rather than zirconium.

Although the powder probably contained but very little free zirconium, it was nevertheless heated in hydrogen, and vapour of iodine was passed over it. An examination of the product gave no satisfactory indications, however, that an iodide of zirconium had been formed.

Inasmuch as the failure to obtain union between the zirconium and iodine might reasonably be ascribed to absence of free zirconium in the above product, it seemed advisable, before attempting any modification of the iodine treatment, to prepare zirconium by some other method and especially by some procedure in which the presence of any appreciable amount of oxygen is avoided. Under the circumstances the method of Berzelius (*Ann. der Phys.*, Pogg., iv., 117), the reduction of potassium fluozirconate with metallic potassium, seemed the most promising, and was therefore employed.

The potassium fluozirconate was prepared from zircon. The zircon was finely ground, sifted through bolting cloth, and digested with concentrated hydrochloric acid until the acid gave no reaction for iron. The powdered zircon, which was now almost perfectly white, was dried and mixed with four times its weight of sodium carbonate. The mixture was fused in an assay crucible furnace, allowed to cool, pulverised, and repeatedly extracted with water. The residue, consisting of zirconia and unattacked zircon, together with some silica and ferric oxide, was heated with concentrated hydrochloric acid, evaporated to dryness, and heated in an air bath to 120° to render the silica insoluble. The dried mass was treated with a little hydrochloric acid, water was added, and the silica and other insoluble matter was filtered off. The filtrate, now containing zirconium chloride and some ferric chloride, was largely diluted with water, and ammonium hydroxide was added until there was formed a slight but permanent precipitate, which was then dissolved by adding as little hydrochloric acid as possible. Sulphur dioxide was then passed into the solution until the liquid smelled strongly of the gas. In many cases a precipitate of basic zirconium sulphite formed at once, but, as the compound seemed to be somewhat soluble in an excess of sulphurous acid, the solution was always boiled for from ten to fifteen minutes to insure complete precipitation. In the reaction free hydrochloric acid is formed, both by the conversion of the zirconium chloride into the basic sulphite and by the reduction of the ferric chloride to the ferrous salt. As this acid would dissolve the zirconium sulphite, it was partially neutralised by the addition, from time to time, of a few drops of dilute ammonium hydroxide. The zirconium precipitate not being wholly free from iron, it was dissolved in hydrochloric acid and again precipitated with sulphur dioxide. The pure zirconium basic sulphite thus obtained was dissolved in hydrochloric acid, and zirconium hydroxide was precipitated

by adding ammonium hydroxide. The well-washed hydroxide was dissolved in hydrofluoric acid, potassium fluoride was added, and the resulting potassium fluozirconate was dissolved in hot water and re-crystallised.

The potassium fluozirconate thus prepared was reduced with metallic sodium, the operation being carried out in a cast-iron crucible. The crucible is cylindrical in form, with an internal diameter of 2 inches and depth of 5 inches. The wall and bottom are over 1 inch in thickness. At the top it has a flange 7 inches in diameter, and is provided with a cast-iron cover 1 inch in thickness, which can be firmly fastened to the flange by means of six one-half inch bolts.

In charging the crucible, sodium chloride, finely ground and thoroughly dried, was first put in to the depth of about an inch and a half, and this was then well pounded down with a wooden plunger to compact the salt and expel the enclosed air. On top of the salt were placed alternate layers of potassium fluozirconate, also thoroughly dried, and metallic sodium, these being pounded down as before. The remaining space in the crucible was then filled with sodium chloride, and, after pounding this down, the top was bolted on and the crucible was heated for about three hours with three triple burners. This heat, however, was not sufficient to raise the crucible to redness.

The crucible was then allowed to cool, and, upon opening it, the charge was found to be so compact that it had to be loosened with a chisel. On treating the mass with water, the metallic zirconium, together with a small amount of the oxide which had formed, settled to the bottom, while the sodium chloride and potassium and sodium fluorides dissolved.

The zirconium and zirconium oxide were separated by first floating off the lighter zirconium with water, and then digesting it with dilute hydrochloric acid at 40° until all of the oxide had been dissolved. The resulting product was a black amorphous powder, which, after washing with water, alcohol, and then with ether, showed no trace of impurity before the spectroscope except a slight amount of sodium.

Vapour of iodine was passed over some of this zirconium heated to dull redness in a current of hydrogen, but with no better success than with the other sample. We then concluded to substitute hydriodic acid gas for the iodine. Considerable difficulty was encountered in finding a suitable method of preparing the gaseous hydriodic acid. That described by Merz and Holzmann (*Ber. d. Chem. Ges.*, xxii., 867) was finally found to answer admirably. It consists in passing dry hydrogen and vapour of iodine through a red-hot tube filled with pumice-stone and freeing the hydriodic acid gas from iodine by passing the gases through cotton.

In treating the zirconium with hydriodic acid gas the following apparatus was used:—

Iodine was placed in a small tubulated flask connected on one side with an apparatus furnishing pure dry hydrogen, and on the other side with a long piece of combustion tubing. The half of this tube nearest the iodine flask was filled with pieces of pumice-stone, and rested in a combustion furnace. The other half, extending beyond the combustion furnace, was filled with cotton. The end of this tube was connected with another combustion-tube resting in a second combustion furnace. The porcelain boat containing the zirconium was placed in this second tube.

The hydrogen was first passed through the whole apparatus for several hours, and then the first furnace was lighted. When the pumice had become red hot the flask containing the iodine was gently heated. The tube containing the zirconium soon became filled with the hydriodic acid gas, whereupon the second furnace was lighted. As the temperature rose, a brownish yellow substance collected in the cold end of the combustion-tube, but as the heat became greater the colour entirely

disappeared, and there remained an amorphous white sublimate. No further sublimate was formed until the tube had almost reached a bright red heat, when there appeared, just beyond the point where the tube was red hot, a white crystalline sublimate, different in appearance from that which first formed. The gas escaping from the end of the tube contained hydriodic acid, hydrogen, some iodine, and a trace of iron, the last probably being present in traces in the zirconium and volatilising as ferrous iodide. The tube was kept at a bright red heat for from three to four hours. The gas was then turned off, and when the boat had cooled considerably the heating of the iodine flask was discontinued. The first furnace was then shut off, and the whole apparatus was allowed to cool in the current of hydrogen.

The material in the boat had changed from a black to a greyish white colour, but a chemical examination showed that it contained very little iodine. The amorphous sublimate which first formed was found not to be zirconium iodide, but to contain chiefly iron and iodine.

The crystalline sublimate which was formed only at a red heat was next analysed. These crystals were found to be insoluble in water, nitric acid, hydrochloric acid, aqua regia, and carbon disulphide. They were decomposed and dissolved by concentrated sulphuric acid; they were also decomposed, but not completely, by concentrated nitric acid, iodide being liberated, and a white powder—insoluble in the nitric acid—remaining. This residue was soluble in concentrated sulphuric acid, and from this solution ammonium hydroxide threw down a white gelatinous precipitate. Upon dissolving this precipitate in hydrochloric acid and dipping turmeric paper into the solution, the orange colour characteristic of zirconium was obtained. The solution gave no reaction for iron.

The zirconium in the compound was quantitatively determined by expelling the iodine by heating a portion of the salt with a mixture of sulphuric, nitric, and nitrous acids, dissolving the residue in concentrated sulphuric acid, diluting with water, and precipitating the zirconium with ammonium hydroxide. The precipitate was washed, dried, and ignited, and the zirconium weighed as the dioxide.

The iodine was determined by fusing some of the compound with about five times its weight of a mixture of potassium and sodium carbonate. The mass was then treated with water, filtered, and after acidifying the filtrate with nitric acid the hydriodic acid was precipitated with silver nitrate and weighed as silver iodide.

The results were—

	Calculated for ZrI_4 .		Found.	
	Per cent.	Per cent.	Per cent.	Per cent.
Zirconium	15.15	15.17	15.00	15.37
Iodine ..	84.85	85.34	85.27	—

The crystals when examined under the microscope proved to be clear, colourless cubes, which showed no double refraction.

When heated for some hours in hydrogen the zirconium tetraiodide becomes black, and iodine and hydriodic acid are formed. Heated in the air the iodide melts and sublimes. A weighed amount was placed in a porcelain crucible, covered with water, and evaporated to dryness. No change in weight, and scarcely any in colour, resulted after two such treatments. This behaviour toward water is surprising, for, from the published descriptions of zirconium tetrachloride and tetrabromide, it was to be expected that the iodide would prove to be a hygroscopic compound easily decomposed by water. It seems, however, to more nearly resemble the fluoride which Deville states to be a colourless crystalline substance, volatile at a white heat, and insoluble in water or acids.—*Journal of the American Chemical Society*, vol. xviii., No. 8.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

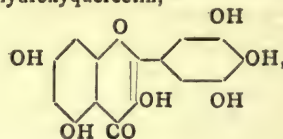
Ordinary Meeting, June 18th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Continued from p. 96).

83. "On the Colouring-matter contained in the Bark of *Myrica nagi*." By A. G. PERKIN and J. J. HUMMEL.

Myrica nagi is an evergreen tree, belonging to the Myricaceæ occurring in the sub-tropical Himalayas, in the Khasia mountains, the Malay Islands, and Japan. The bark, which is used as a tanning agent, and occasionally for medicinal purposes, was found to contain a yellow colouring-matter. This formed yellow needles, closely resembling quercetin, having the formula $C_{15}H_{10}O_8$, and yielding compounds with mineral acids, $C_{15}H_{10}O_8H_2SO_4$, $C_{15}H_{10}O_8HBr$, $C_{15}H_{10}O_8HCl$, and $C_{15}H_{10}O_8HI$, orange to orange-red needles, decomposed by water into the free acid and colouring matter. In strong solutions of alkali it dissolves with an orange colour, which, on dilution and exposure to air, becomes first green, then deep blue, and finally red-violet. It dyes shades which, in their general character, closely resemble those produced by quercetin and fisetin. The acetyl derivative, $C_{15}H_4O_8(C_2H_3O)_6$, colourless needles, m. p. 203—204°, and the benzoyl compound, $C_{15}H_4O_8(C_7H_5O)_6$, m. p. 233—236°, are described. With fused alkali it yields phloroglucol and gallic acid, and with bromine a compound (orange-brown needles, m. p. 235—240°), the analytical numbers for which agree with the formula $C_{15}H_6O_8Br_4$. This is probably a tetrabromo-derivative of the colouring-matter, but on account of its somewhat peculiar properties, it will require further examination. The results of this investigation show that this colouring-matter, for which the name *myricetin* is proposed, is most probably an hydroxyquercetin,—



and experiments with its alkyl ethers will be carried out to confirm this point. Its colour reactions with dilute alkali are probably due to the oxidation of the pyrogallol nucleus it contains. The amount of colouring-matter, isolated by the method described, varied from 0.23 to 0.27 per cent, and the amount of tannin it contained, estimated under the direction of Mr. H. H. Procter, Lecturer on Leather Industries, Yorkshire College, was found to be 27.30 per cent.

84. "Preliminary Note on a New Base derived from Camphoroxime." By MARTIN O. FORSTER, Ph.D.

Camphoroxime undergoes no change when treated with boiling methylic iodide in a reflux apparatus, but on heating it with this agent in sealed tubes at 170—180°, the hydriodide of a new base is produced, along with campholenitrile. The quantity of the salt obtained from 15 grms. of camphoroxime and 30 grms. of methylic iodide was 9.5 grms.

The base is a colourless limpid oil, having the odour of piperidine; it boils at 206—207°, and is markedly levorotatory. It is tertiary in character, and analysis points to the formula $C_{12}H_{19}N$ as representing its composition. (Found: C = 81.06; H = 10.66. Calculated for $C_{12}H_{19}N$, C = 81.35; H = 10.73 per cent.)

The platinichloride, $(C_{12}H_{20}N)_2PtCl_6$, crystallises from alcohol in magnificent orange needles, and melts, decomposing at 214.5°; the hydriodide, $C_{12}H_{19}N, HI$, separates from water in lustrous straw-yellow six-sided plates, and

effervesces vigorously when heated at 285°. The *picrate* and *mercurichloride* are well-defined salts, melting at 190° and 126—128° respectively, whilst the *chromate* crystallises in microscopic pale brown square plates, becoming purple on exposure to light. Incidentally, the *hydrobromide*, and the *acetyl* and *methyl* derivatives of camphor-oxime have been obtained.

85. "The Rotation of Aspartic Acid." By B. M. C. MARSHALL, A.R.C.S.

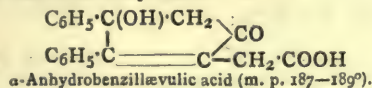
In view of the contradictory statements concerning the rotation of aspartic acid in aqueous solution, the author has re-examined the subject.

Landolt (*Ber.*, xiii., 2334) and Becker (*Ber.*, xiv., 1035) obtained a *lævo*-rotation for aspartic acid, prepared from ordinary asparagine. Piutti (*Ber.*, xix., 1691), on the other hand, states that ordinary asparagine yields *dextro*-aspartic acid, which is convertible into ordinary *lævo*-malic acid, while the *dextro*-asparagine yields *lævo*-aspartic acid, which gives *dextro*-malic acid.

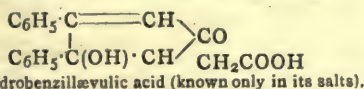
The results obtained by the author confirm the observations of Piutti. The solubility of the aspartic acid in water was found to be in agreement with the results of Pasteur, Guareschi (*Jahresber.*, 1876, 777), and Engel (*Compt. Rend.*, cvi., 1736), and to be much less than that deduced from Becker's data.

86. "Synthesis of Pentacarbon Rings. Part III. Condensation of Acid with Lævulic Acid." By FRANCIS R. JAPP, F.R.S., and T. S. MURRAY, D.Sc.

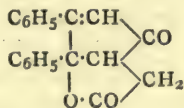
When benzil and lævulic acid are heated with a solution of caustic potash in dilute alcohol, they condense to form two isomeric compounds.



and—

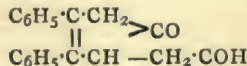


These two *diphenylhydroxycyclopentenylacetic acids* are allied to anhydracetonebenzil, which is a *diphenylhydroxycyclopentenone* (Japp and Lauder, *Proc. Chem. Soc.*, 1896, 107). The α -acid is stable; the β -acid, when liberated from its salts, spontaneously changes into the lactone,—



(m. p. 151—152°).

Both the α -acid and the lactone of the β -acid, when boiled for from one to two minutes with fuming hydriodic acid, are converted into *diphenylcyclopentenonylacetic acid*,—



(m. p. 126—127°), a change in the position of the double bonds occurring during the process. The latter acid, on oxidation with sodium hypobromite, yields a mixture of *diphenylmaleic* and *diphenylfumaric acids*.

Oximes and other derivatives of the foregoing compounds have also been prepared.

87. "Absorption of Dilute Acids by Silk." By JAMES WALKER and JAMES R. APPLEYARD.

When silk is dyed with picric acid a real equilibrium is attained which is independent of the original distribution of the materials. If the equilibrium concentration of the picric acid in the silk be denoted by s , and in the water by w , the relation—

$$s/\sqrt{w} = \text{const.}$$

exists between these magnitudes. This formula would indicate, according to the solid solution theory of dyeing, that the weight of the molecule of picric acid dissolved in the water would be n times that of the molecule of picric acid "dissolved" in the silk; but this we know to be incorrect, as n is greater than unity, and the molecular weight of picric acid in water is the smallest consistent with its formula.

When other solvents than water are used the rate and amount of dyeing with picric acid seem to be connected with the dissociative power of the solvent. Silk will not take up picric acid from benzene or from carbon tetrachloride, but does so readily from alcohol, less readily from ether and acetone. The ratio of the final concentrations of aqueous and alcoholic solutions of picric acid required to dye silk to a given standard was found to be approximately the ratio of the solubilities of picric acid in water and in alcohol.

A comparison of the extents to which the various acids are absorbed by silk shows that the acids fall into two classes—the aromatic acids where the absorption is great, and the non-aromatic acids where the absorption is relatively small. In each class there is a rough parallelism between the strength of the acids and the amount absorbed. The addition of calcium benzoate to a solution of benzoic acid greatly diminishes the strength of the acid, and the absorption also is thereby much diminished.

If dyeing were a pure chemical addition of the dye to the fibre, the theory of mass-action predicts that the equilibrium concentration of the dye-bath should be constant at any given temperature independently of the quantities of material taken. This is not known to be the case for actual dyeing, but it was experimentally verified by "dyeing" diphenylamine brown with picric acid from aqueous solution.

88. "Position-isomerism and Optical Activity; the Methylc and Ethylic Salts of Ortho-, Meta-, and Paraditoluyltartaric Acid." By PERCY FRANKLAND, Ph.D., F.R.S., and FREDERICK MALCOLM WHARTON, A.I.C.

The authors have commenced the systematic study of the connection between position-isomerism and rotatory power in optically active substances containing the benzene ring. The present paper contains an account of the preparation and properties of the methylc and ethylic salts of the three isomeric ditoluyltartaric acids. These substances were obtained by the action of the three toluy chlorides on methylc and ethylic tartrates respectively. With the exception of the ethylic salts of the diortho- and dimeta-toluyltartaric acids, they were all obtained as beautifully crystalline bodies, the two ethylic salts in question only as viscid liquids. All six compounds are powerfully *lævorotatory*, the methylc salts more so than the corresponding ethylic ones, and the para-compounds have the highest, the ortho- the lowest, and the meta- an intermediate rotation. As regards other physical properties, in the case of the methyl compounds, all of which are solids at the ordinary temperature, the para- also has the highest, the ortho- the lowest, and the meta-compound an intermediate melting-point, whilst the density is distinctly greatest in the case of the ortho-compounds, the meta- and para-compounds having almost exactly equal densities. In all cases the rotatory power was determined in the liquid state, no use being made of solutions, and the rotations were compared over wide ranges of temperature. With rise in temperature the *lævorotatory* power is in all cases diminished, and since the *lævorotation* is conditioned by the presence of the aromatic groups (methylc and ethylic tartrates being *dextrorotatory*), the dominant influence of these groups is reduced with increasing temperature; a perfectly analogous phenomenon has already been shown by one of the authors to take place in the case of the dibenzoylglycerates (*Trans.*, 1896, 106). Moreover, as the *lævorotation* is conditioned by the toluyl groups, it follows from a comparison of the rotations of the compounds described that the meta-toluyl

group has a higher rotatory value than the ortho-, and the para- an even higher one than the meta-.

89. "Double Sulphides of Gold and other Metals, or the Action at a Red Heat of Sulphur upon Gold when Alloyed with other Metals." By J. S. MACLAURIN, B.Sc., University College, Auckland, New Zealand.

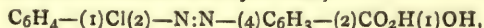
It is shown that when alloyed with silver, lead, copper, or iron, gold is readily converted into a sulphide by the action of sulphur vapour on the melted alloys. Analyses of the compounds so prepared are given which prove that the gold sulphide has the formula Au_2S .

90. "The Relative Weights of Gold and Silver dissolved by Potassium Cyanide Solutions from Alloys of these Metals." By J. S. MACLAURIN, B.Sc.

The author finds that gold and silver are dissolved by solution of potassium cyanide from an alloy of these metals in the proportions by weight in which they exist in it. He shows that this is the ratio of their atomic volumes, and deduces it from the results previously obtained by him (*Trans.*, 1895, 199).

91. "The Three Chlorobenzeneazosalicylic Acids." By J. T. HEWITT, Ph.D., and H. E. STEVENSON.

Orthochlorobenzeneazosalicylic acid,—



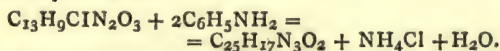
prepared by the addition of diazotised orthochloraniline hydrochloride to an alkaline solution of salicylic acid, forms yellow or buff aggregates of small crystals (m. p. 194°).

Besides metallic salts, the methyl and ethyl esters are described. Methyl orthochlorobenzeneazosalicylate, m. p. 109°. Ethyl orthochlorobenzeneazosalicylate, m. p. 90—96°.

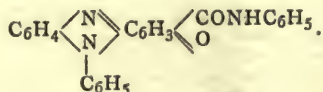
Attempts to remove hydrochloric acid by inorganic bases were fruitless, and diphenelenazo derivatives were not produced.

Boiled with aniline, in a flask provided with a reflux tube, a sublimate of ammonium chloride was observed, the chief product of the reaction being a substance of the formula $C_{25}H_{17}N_3O_2$. To effect its isolation, the contents of the flask are freed from aniline by steam distillation, subsequent treatment with soda removes an acid probably having the formula $C_{10}H_{12}N_2O_3$; after washing with hydrochloric acid, the residue is dissolved in chloroform and precipitated by ligroin as a violet crystalline powder.

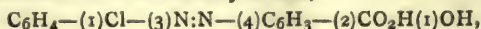
The formation of the substance $C_{25}H_{17}N_3O_2$ may be thus represented:—



The substance possesses neutral properties, and is probably the anilide of a benzeneindulonecarboxylic acid,—



Metachlorobenzeneazosalicylic acid,—

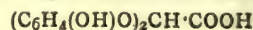


has been previously described (*Ber.*, 1894, xxviii., 803). An account is now given of some of its metallic salts. Methyl metachlorobenzeneazosalicylate forms yellow needles which melt at 114°. Ethyl metachlorobenzeneazosalicylate, m. p. 102—103°. Parachlorobenzeneazosalicylic acid, $C_6H_4-(1)Cl-(4)N:N-(4)C_6H_3-(2)CO_2H(1)OH$, was prepared in the usual manner; it melts at 237°. The potassium, ammonium, silver, and barium salts are described. Methyl parachlorobenzeneazosalicylate, m. p. 152°. Ethyl parachlorobenzeneazosalicylate, m. p. 113°.

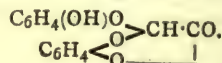
For purposes of comparison the methyl and ethyl esters of benzeneazosalicylic acid (Stebbins, *Ber.*, 1880, xiii., 716) have also been prepared. Methylbenzeneazosalicylate, m. p. 106°. Ethylbenzeneazosalicylate. m. p. 88—89°.

92. "Condensation of Chloral with Resorcinol." By J. T. HEWITT, M.A., D.Sc., Ph.D., and F. G. POPE.

H. Causse studied the condensation of chloral with resorcinol in dilute aqueous solution under the influence of sodium hydrogen sulphate (*Bull. Soc. Chim.*, [3], iii., 861—867). In this manner he obtained a colourless compound of the formula $C_{14}H_{12}O_6$; whilst working with hot solutions, yellow crystals of the formula $C_{14}H_{10}O_5$ were obtained. He assigned to these two substances the following constitutional formulæ:—



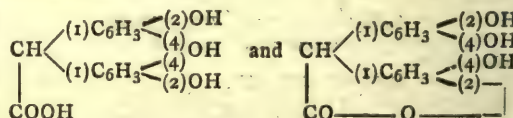
and—



The authors of the present communication have studied the latter substance, and find that it furnishes a triacetyl derivative (m. p. 152°) crystallising in glittering leaflets. The substance $C_{14}H_{10}O_5$ dissolves in cold alkalis with an intense purple colour which disappears on warming, salts of the type $M \cdot C_{14}H_{11}O_6$ being produced. The purple alkaline solution of the formula $C_{14}H_{10}O_5$ gives a precipitate on acidification, solutions of salts $M \cdot C_{14}H_{11}O_6$ only on boiling for some time.

The conclusion can be drawn that the compound $C_{14}H_{10}O_5$ is the lactone of an acid, $C_{14}H_{12}O_6$, which is itself readily soluble in water. This acid must contain four hydroxyl groups, and is, therefore, tetrahydroxy-diphenylacetic acid.

Probably the acid and lactone possess the following constitutional formulæ:—



93. "The Atomic Weight of Japanese Tellurium." By MASUMI CHIKASHIGÉ, B.Sc., Imperial University, Japan.

A re-determination of the atomic weight of tellurium has been made by means of its tetrabromide, and by closely following Brauner in all the details. The result has been to get, in the three experiments made, the numbers 127.57, 127.61, and 127.58, which, therefore, agree with his in making the atomic weight 127.6. This work was undertaken by the advice of Dr. Divers, in order to ascertain whether tellurium found under mineralogical conditions quite unlike those pertaining to the tellurium employed by Brauner, Staudenmaier, and all others who have investigated the subject, has the same atomic weight as the latter. That, as is well known, occurs in Hungary and elsewhere, in union with bismuth, gold, silver, &c., while the tellurium employed in this research was obtained from the red native sulphur, or telluro-sulphur, of Japan, discovered and described in 1883 by Divers, Shimose, and Shimidzu. It is extremely improbable that, if the substance known as tellurium is compound, as it has been considered to be by Brauner, its composition should be identical when occurring in association with sulphur as a sulphur-like body in Japan, as when occurring in metallic combination in Europe or America. Since Staudenmaier has got the same atomic weight for tellurium of European origin as that found by Brauner, but by a totally different method, and that the author has again got the same atomic weight by Brauner's process, but working on a tellurium of quite dissimilar origin, the point may be regarded as settled that its atomic weight exceeds that of iodine. Its occurrence with sulphur and selenium in the Japanese mineral at the same time furnishes additional proof that it belongs to the sulphur group.

ADDENDUM, BY EDWARD DIVERS.—The case of tellurium and iodine, with atomic weights in the reverse order of their places in the periodic series, is not the only one. Cobalt belongs, undoubtedly to the second division of

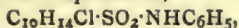
Group VIII., and nickel to the third division, according to both Mendeleeff and Lothar Meyer; yet all the elaborate work done on the subject has left cobalt with an atomic weight slightly higher than, or at least equal to, that of nickel. Hence we find in most books cobalt and nickel misplaced in the reproduction of Mendeleeff or Meyer's table. It is to be hoped no one will venture now to misplace tellurium and iodine.

94. "Derivatives of Camphene Sulphonic Acids." By ARTHUR LAPWORTH and FREDERIC STANLEY KIPPING.

The two chlorocamphenesulphonic chlorides obtained as by-products in the sulphonation of camphor (compare *Proc.*, 1895, 57) have been submitted to a further examination. Although no experimental proof of their relationship to camphene has yet been obtained, their characterisation has now been completed, and a number of new derivatives have been prepared from them.

α -Chlorocamphene sulphochloride, $C_{10}H_{14}Cl \cdot SO_2Cl$, is dimorphous, as was at first expected (*loc. cit.*). It crystallises from light petroleum or cold methylic alcohol in massive transparent anorthic prisms or plates, which melt at $83-84^\circ$; from hot methylic alcohol it is deposited in small orthorhombic tables which melt at $87-88^\circ$. The latter modification is also obtained when the melted substance is quickly cooled, and undergoes gradual reversion to the anorthic modification at the ordinary temperature. Both forms have been goniometrically measured.

α -Chlorocamphene sulphanilide,—



crystallises in small flattened needles, which probably belong to the anorthic system; it is readily soluble in alcohol, but only sparingly soluble in ether or chloroform; it melts and decomposes about $232-234^\circ$.

α -Chlorocamphene sulphonic acid, $C_{10}H_{14}Cl \cdot SO_3H$, crystallises from ether in beautiful glistening elongated plates; it dissolves sparingly in ether and in chloroform, but is insoluble in petroleum. When heated it gradually darkens, and at $264-265^\circ$ swells up and evolves gases, finally forming a dark-coloured liquid mass.

β -Chlorocamphene sulphochloride, $C_{10}H_{14}Cl \cdot SO_2Cl$, crystallises from anhydrous methylic alcohol in long needles which belong to the tetragonal system, and melts at $83-84^\circ$; the low melting-point (78°) originally observed was probably due to some slight admixture with the isomeric sulphochloride, the latter being almost impossible to eliminate by crystallisation from petroleum.

β -Chlorocamphene sulphanilide, $C_{10}H_{14}Cl \cdot SO_2 \cdot NHC_6H_5$, is slightly soluble in hot water, and crystallises from dilute alcohol in branched aggregates of plates; it melts at $101-103^\circ$.

β -Chlorocamphene sulphonic acid, $C_{10}H_{14}Cl \cdot SO_3H$, is readily soluble in water, and crystallises from ether in minute ill-defined leaflets; it melts at $73-74^\circ$, and decomposes and evolves gases at about 142° . When the solution of this acid is evaporated to dryness on the water-bath, and the residue extracted with water, a substance remains undissolved which is isomeric with β -chlorocamphene sulphonic acid. This compound crystallises from methylic alcohol in well-defined plates, which aggregate on pressure to a camphor-like mass; it melts at $183.5-184.5^\circ$. It is not altered by hot aniline, but is gradually dissolved by boiling baryta water, forming an ill-defined salt. Its behaviour is in accordance with the supposition that it is the lactone of a hydroxy-sulphonic acid.

95. "Iodoso- and Iodoxy-Benzaldehydes." By VICTOR MEYER and T. S. PATTERSON.

It is shown that *m*- and *p*-iodoso- and iodoxy-benzaldehydes are much easier to prepare than *o*-iodoso-benzaldehyde, which is contrary to the hitherto observed rule.

The preparation of the following new substances is described:—

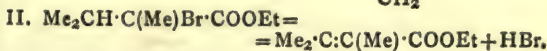
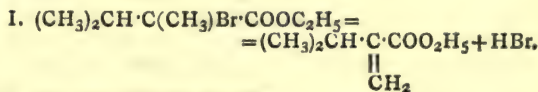
m-Iodo-benzaldehyde, m. p. 57° , *m*-Iodo-benzaldehyde-bichloride. *m*-Iodoso-benzaldehyde; decomposes (*circa*)

190° . *m*-Iodoso-benzaldehyde-acetate, m. p. 157° . *m*-Iodoxy-benzaldehyde. *p*-Iodo-benzaldehyde-bichloride. *p*-Iodoso-benzaldehyde; decomposes at 115° . *p*-Iodoxy-benzaldehyde; decomposes at 216° . *o*-Iodo-benzaldehyde-bichloride. *o*-Iodoso-benzaldehyde; decomposes at $205-210^\circ$. *o*-Iodo-benzaldoxime, m. p. $107-108^\circ$. *m*-Iodo-benzaldoxime, m. p. $62-63^\circ$. *p*-Iodo-benzaldoxime, m. p. 111° . *o*-Iodo-benzaldehyde-phenylhydrazone, m. p. 79° . *m*-Iodo-benzaldehyde-phenylhydrazone, m. p. 155° . *p*-Iodo-benzaldehyde-phenylhydrazone, m. p. 121° .

96. " α -Isopropylglutaric Acid." By W. H. PERKIN, jun., F.R.S.

During the course of experiments on derivatives of glutaric acid, the author had occasion to carefully study the action of alkalis on ethylic methylisopropyl- α -bromacetate, and also the action of this ethereal salt on the sodium derivative of ethylic malonate.

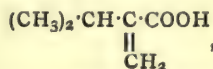
$(CH_3)_2CH \cdot C(CH_3)Br \cdot COOC_2H_5$, ethylic methylisopropyl- α -bromacetate, was prepared by brominating methylisopropylacetic acid in the presence of phosphorus, and pouring the product into alcohol; it boils constantly at 130° (100 m.m.). When heated with quinoline, this ethereal salt yields a mixture of the ethereal salts of α -isopropylacrylic and of trimethylacrylic acids, elimination of hydrogen bromide taking place in two directions, thus:—



And, when digested with alcoholic potash, the bromo-ethereal salt yields a mixture of the above acrylic acids, together with small quantities of methylisopropyl- α -hydroxyacetic acid.

Trimethylacrylic acid, $(CH_3)_2C \cdot C(CH_3) \cdot COOH$, crystallises in colourless prisms, and melts at 71° ; it combines with bromine, yielding $\alpha\beta$ -dibromotrimethylpropionic acid, $(CH_3)_2CBr \cdot CBr(CH_3) \cdot COOH$ (m. p. 190°), and with hydrogen bromide and hydrogen iodide with formation of $(CH_3)_2CBr \cdot CH(CH_3) \cdot COOH$, β -bromotrimethylpropionic acid (m. p. 79°), and $(CH_3)_2C \cdot Cl \cdot CH(CH_3) \cdot COOH$, β -iodotrimethylpropionic acid (m. p. 81°) respectively.

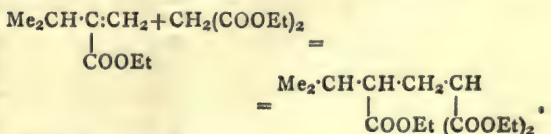
α -Isopropylacrylic acid,—



has not been obtained in a pure state.

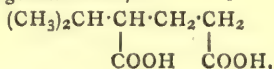
$(CH_3)_2CH \cdot C(OH) \cdot CH_3 \cdot COOH$, methylisopropyl- α -hydroxyacetic acid, crystallises in colourless prisms and melts at $75-76^\circ$.

Condensation of Ethylic Isopropylacrylate with the Sodium Compound of Ethylic Malonate.—When the mixed ethereal salts of isopropylglutaric acid and trimethylglutaric acid (as obtained by the action of quinoline on ethylic methylisopropyl- α -bromacetate) are digested with the sodium derivative of ethylic malonate in alcoholic solution, condensation takes place, curiously enough, only in the case of the former substance.

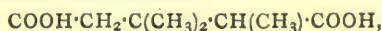


The ethylic isopropylpropanetricarboxylate thus formed is a thick colourless oil which boils constantly at 209° (45 m.m.), and, on hydrolysis, yields the corresponding isopropylpropanetricarboxylic acid; this acid melts at 165° with decomposition into CO_2 and α -isopropylglutaric acid.

α-Isopropylglutaric acid,—



melts at 94—95°, and in its properties shows considerable resemblance to the isomeric—



αββ-trimethylglutaric acid, which Balbiano (*Ber.*, 1895, xxviii., 1507) obtained from the products of the oxidation of camphoric acid with cold potassium permanganate. It yields an ethereal salt which boils at 158—160° (45 m.m.), an anhydride, $\text{C}_8\text{H}_{12}\text{O}_3$ (m. p. 53°), an anilic acid, $\text{C}_{14}\text{H}_9\text{NO}_3$, which melts at 159°, and it is oxidised by chromic acid with formation of acetic and succinic acids.

Action of Ethylic Methylisopropyl α-Bromacetate on the Sodium Compound of Ethylic Malonate.—This reaction was studied under a variety of conditions, using alcohol and xylene as solvents, but in all cases the product was found to be identical with the ethylic isopropylpropanetricarboxylate, obtained, as described above, by the condensation of ethylic isopropylacrylate with the sodium derivative of ethylic malonate. During this reaction the ethylic methylisopropylbromacetate is obviously first converted into ethylic isopropylacrylate, which then condenses with the sodium compound of the ethylic malonate in the manner described above.

(To be continued).

NOTICES OF BOOKS.

Commercial Organic Analysis. A Treatise on the Properties, Proximate Analytical Examination, and Modes of Assaying the Various Organic Chemicals and Products employed in the Arts, Manufactures, Medicine, &c., with Concise Methods for the Detection and Determination of their Impurities, Adulterations, and Products of Decomposition. By ALFRED H. ALLEN, F.I.C., F.C.S., Past President of the Society of Public Analysts, Public Analyst for the West Riding of Yorkshire, the City of Sheffield, &c. Second Edition, Revised and Enlarged. Vol. iii., Part 3. London: J. and A. Churchill. 1896. 8vo., pp. 508.

MR. ALLEN'S *magnum opus* approaches its conclusion, and certainly betrays no signs of deterioration in the quality of its matter. The present volume contains the conclusion of the vegetable alkaloids, the non-basic vegetable bitter principles, the animal bases, the animal acids, and cyanogen with its derivatives.

Among the alkaloids we find carpine, the basic principle of *Carica papaya*, which is correctly described as a Javanese tree, in contradiction to the common error which makes it a native of South America. It must not be confounded with the ferment papain. Colchicine, dear to the heart of certain quacks, is described, not without a caution as to its poisonous and uncertain effects.

The adulterations of pepper appear to be numerous. In a note we read that the Somerset House chemists allow 3½ per cent of sand, and an additional 7 per cent of mineral matter is stated to be allowed by "public analysts and writers of authority." Mr. Allen pronounces such allowances quite indefensible.

Solanine and solanidine are met with in potatoes which are either unripe or are sprouting. They have been found in the residues of a German distillery, and have poisoned cattle.

The use of chrome-yellow for the sophistication of mustard seems to be a sin of the past. But Martius yellow has been found in mustards of French, German, and American manufacture.

A remarkable fact is that solutions of *digitalis* are poisons to plants. The *digitalis* poisons occur also in the leaves of the oleander.

Under the heads "Ouabain" and "Antiarin" we find a very interesting survey of the arrow-poisons used by various savage tribes.

It is a curious fact that *Pyrethrum carneum* and *P. roseum* are probably present in "insect-powders," which, by the way, are not harmless to higher animals.

Chirette or chiraytor figures in certain proprietary medicines, and is also used as a substitute for hops.

Full justice is done to the subject of the ptomaines, including the chemistry of putrefaction, which is now understood as a fermentation in nitrogenous organic matters set up in presence of bacteria. It is remarked, on the authority of Brieger, that the formation of a highly toxic ptomaine corresponds with the disappearance of choline. Some of these products of putrefaction—such as cadaverine, putrescine, and saprine—are not poisonous, but nydaine is a highly poisonous diamine. The typhoid bacillus of Eberth is not produced in putrefaction, but there are found in the excreta of the patients traces of a base which proves rapidly fatal.

The odour of some ptomaines resembles that of syringa, and is so persistent that it has been observed in products of ancient putrefaction, found in bone-caves. But in other cases it is found that these products of putrefaction are most dangerous which do not attract attention by odours or by change of colour or texture.

There is the very suggestive caution laid down that "ptomaines produced by putrefactive decomposition after death have been mistaken for poisonous vegetable bases administered during life."

Mytilotoxine, $\text{C}_6\text{H}_{15}\text{NO}_2$, has been obtained from putrescent mussels, and is supposed to be the agent in mussel poisoning. Brieger's typhotoxine is supposed to be the poison of typhus fever; and tetanine, $\text{C}_{13}\text{H}_{30}\text{N}_2\text{O}_4$, is believed, as its name indicates, to be the active agent in tetanus.

Vaughan's tyrotoxicon is obtained from stale milk, ice-creams, and decomposing cheese. It produces symptoms identical with those of *cholera infantum*. It is highly remarkable that cod-liver oil yields two poisonous ptomaines—morrhaine, $\text{C}_{19}\text{H}_{27}\text{N}_3$, and aselline, $\text{C}_{25}\text{H}_{32}\text{N}_4$.

There is a notice of the arsenical ptomaines suspected to have been present in the *Aqua Tofana* and *Acquetta di Perregia* celebrated in the history of mediæval secret poisoning. Husemann suggests that similar compounds may be generated in the size and paste used in fixing arsenious papers on the walls of bed-rooms.

Space unfortunately warns us to curtail our further survey of this most valuable and interesting book, but we cannot refrain from quoting the collapse of prisoner's counsel in the trial of Tawell. The learned advocate suggested that the prussic acid detected in the stomach of the deceased might be derived from apple-pips, and dropped the subject when told that "about a peck" might suffice.

The Glasgow and West of Scotland Technical College Calendar for the Session 1896—97. Glasgow: Printed for the College.

THE Glasgow and West of Scotland Technical College reminds us in many respects of the Polytechnicum of Zurich, of Aix-la-Chapelle, &c. It is, however, more contaminated with examinationism, to which we Britons still cling "like a dormant bat to a dead bough," despite its grand break-down, civil and military, in the land where it took its origin.

The College seems to have been formed by the coalescence of what was formerly known as the Andersonian University, the Young Laboratory, and Allan Glen's School.

The Freeland chair of Chemistry is at present filled by Prof. Henderson. It has a junior and a senior course of chemistry, inorganic and organic, all arranged for students preparing for certain experiments here specified. Now the chemical classes at the Aix-la-Chapelle, or the

polytechnics, are adapted simply for students seeking to acquire a sound knowledge of chemical science, and we venture to say that they answer the purpose.

The "Freeland" Laboratory is open daily (Saturdays excepted) throughout the academical year, from 9 a.m. to 5 p.m. We are glad to find that there is a special course of demonstration in Spectrum Analysis.

The "Young" chair of Technical Chemistry is filled by Prof. Mills. We do not see whether the students, like the rivals in Germany and Switzerland, have the opportunity afforded them of visiting the different manufacturing establishments which are here referred to. There is a course for the construction and use of chemical plant which should prove highly valuable.

The course of technical organic chemistry, 21 lectures, will begin on Wednesday, October 7th.

Among subsidiary courses is one on dyeing processes, and one on oils, paints, and varnishes, including the conversion of pigments into paints. There is also a special photographic department, and a department for metallurgy and mineralogy conducted by Prof. Sexton.

The scientific principles of agriculture are taught by Prof. Wright in a course of 100 lectures. Agricultural botany is taught by Mr. McAlpine, and economic entomology by Mr. J. F. X. King.

There is also an evening department of the College, in which natural philosophy is taught by Prof. Blyth, chemistry by Prof. Henderson, technical chemistry by Prof. Mills, and agriculture by Prof. Wright. Dr. Barlow lectures on physiology and hygiene.

A course of lectures on music seems to us strangely out of place in an establishment like the Glasgow College. On the Continent, where the study of music is not neglected, it is taught in Conservatoriums, establishments perfectly distinct from the Universities.

In our opinion the Technical College might rival, or even surpass, any foreign Polytechnicum if certain departments were deleted, and if the time and brain-power of the students were not frittered away in preparing for examinations.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Analytische Chemie.
Vol. xxxv., Part 2.

Micro-chemical Distinction between Cinchonidine and Hociinchonidine.—H. Behrens.

General Volumetric Determination of the Metals Precipitable by Fixed Alkalis, Caustic or Carbonated.—Prof. Dr. Ruos.—Already inserted.

Examination of Fine Spirit for the Determination of Fusel Oil.—A. Stutzer and R. Maul.—The procedure employed is an improvement on that of Roscoe. It consists firstly in a concentration of the fusel by eliminating a portion of the alcohol, which must be regarded as free from fusel, or as containing only minimum traces. The next step is to ascertain the specific gravity and dilute the liquid to 30 per cent by volume. The author then gives an account of the apparatus for shaking out with chloroform, of charging the apparatus, and of the manner of shaking out.

Valuation of Benzidin and Toluidin.—W. Vaubel.—Already inserted.

Behaviour of the Naphthols and Naphthylamines with Nascent Bromine.—W. Vaubel.

Peculiar Relations of Solubility in Barium Sulphate.—R. Fresenius and E. Hintz.

Iodine Number and Index of Refraction of Cacao Butter.—Dr. A. Strohl.—The iodine number of pure cacao butters of different origin, degree of ripeness, &c., vary from 32.8 to 41.7. The indices of refraction, determined at 40°, vary from 1.4565 to 1.4578. A cacao butter having a low iodine number will have as a rule a low index of refraction.

Hydrometer Pipette.—Greiner.—This instrument, which is patented, is shown in the figure accompanying the paper.

Process for Dissolving Ignited Iron Oxide and other Metallic Oxides.—Hugo Borntrager.—Already inserted.

Gas Analytical Methods and Apparatus.—W. Fresenius (with the co-operation of W. Schranz).—These include figures and descriptions of the devices of C. Kippenberger, of F. Fischer, G. Neumann, of W. Thörner, of Binder (*Chemiker Zeitung*), of Adeney (*CHEMICAL NEWS*), of W. Younger (*Journ. Soc. Chem. Industry*), of Wanklyn and Cooper (*CHEMICAL NEWS*), pronounced useless by L. L. de Koninck (*Zeit. für Angew. Chemie*) and others.

Determination of the Halogens.—C. Schierholz (*Monatshefte für Chemie*).

Solubilities of the Silver Haloids in Organic and Inorganic Solvents.—E. Valenta (*Monatshefte für Chemie*).

Gas-volumetric Determination of Free Iodine.—A. Baumann.—The author shows that his method, above all, requires a rapid mixture of the alkaline solution of hydrogen peroxide with the solution of iodine, in order that the latter may become quickly alkaline in its whole extent, and no higher oxidation of the hypiodous acid can ensue. According to Baumann's directions, we bring the solution into rotatory movement *before* mixture; incline, then, the generating vessel quickly by about 90°, so that the entire quantity of the alkaline solution of hydrogen peroxide can mix with the solution of hydrogen, and turn the liquid in the slanting position of the glass for about five seconds. If we then shake the entire liquid for ten seconds, the analysis is completed, and the generating apparatus is returned to the cooling water. Every analysis is to be regarded as worthless in which a longer time—say, about one minute—is required for shaking out the gases.

Action of Nascent Bromine upon Benzene.—W. Vaubel (*Journ. Prakt. Chemie*).

Recognition of Indoles and Indol Carbonic Acids.—A. Angeli (*Gazzetta Chim. Italiana* and *Journ. Chem. Society*).—The author fuses traces of the substance in a small glass tube with dehydrated oxalic acid. There appears a beautiful colour and the melted product dissolves in acetic acid. Indol and its aliphatic homologues yield a red colouration, whilst with α -phenylindol a violet is produced.

Determination of Chlorine in Organic Products, e.g., in Urine.—G. Meillièrre (*Journ. Pharm.*).—The author evaporates the substance to dryness with an equal quantity of a 20 per cent solution of calcium nitrate in a platinum capsule. A slight ignition of the residue suffices to destroy the carbonaceous compounds. The watery extract of the residue is free from phosphates. We acidulate slightly with dilute sulphuric acid, and add some calcium carbonate in order to decolourise the liquid. In the neutral colourless filtrate the chlorine can be determined in the usual manner, using potassium chromate as indicator.

Volumetric Determination of Halogens in Organic Substances.—F. W. Küster.—The author, in opposition to J. Walker and J. Henderson (*CHEMICAL NEWS*), states that he has always obtained inaccurate results with the process of Carius as modified by Volhard. Walker and Henderson now show that a part of the silver nitrate is absorbed by the glass only if the decomposition is effected

at too high a temperature (320–340°), as was done by Küster, and the quantity of fuming nitric acid is too small. For most haloidiferous organic substances it is sufficient to heat the tubes to 250–260° for three hours, taking to 0.1 grm. of the substance 2 c.c. nitric acid of specific gravity 1.5. The action of the excess of silver nitrate is then completely avoided, and the results agree with those obtained by the gravimetric method.

Elementary Analysis with the Use of Lead Chromate.—Bruce Warren—From the *CHEMICAL NEWS* (vol. lxxi., pp. 143, 152).

Determination of Nitrogen in Nitriferous Manures.—W. E. Garrigues.—From the *CHEMICAL NEWS* (vol. lxxi., p. 41).

Determination of Nitrogen in Arable Soils.—W. Dafer (Experimental Station Record and Journ. Chem. Society).—In order to avoid the troublesome bumping of the liquid, the author proposes to effect the distillation of the ammonia produced with the introduction of watery vapour. If the soil contains a large quantity of insoluble constituents, it is well to filter after opening up the specimen with sulphuric acid.

Determination of Nitric Nitrogen in Presence of Organic Nitrogen.—Th. Pfeiffer and H. Thurmman (*Land. Versuchsstationen*).

Determination of Sugars.—Lasche (*Biedermann's Central Blatt and Journ. Chem. Soc.*).

Determination and Separation of small Quantities of Methylic and Ethylic Alcohols.—L. Prunier.—From the *Journal of the Chemical Society and the Journ. Pharm.*

Separation of Ethylic Alcohol from Acetic Acid, Methylic Ether, Methyl Acetate, Aldehyds, Phenols, &c.—Maxime Cair-Mantrand.—From the *Comptes Rendus*.

Examination of and Conclusion on Wine.—A number of methods collated by W. Fresenius, assisted by L. Grünhut.

Examination of Balsam of Peru.—Otto Schade (*Pharm. Zeitung*).—The author finds that the yellow colouration prescribed as a test by the Pharm. Germanica on shaking up with petroleum benzin, evaporating off the latter substance from the filtrate, and adding a few drops of crude nitric acid, does not in all cases appear. But if the petroleum-ethereal extract, after evaporation, is further heated on the water-bath for ten to twelve minutes, the required yellow colour appears. Gehe and Co. prefer the determination of the cinnaein as proposed by Flückiger.

Recognition of Fatty Oils in Balsam of Copaiva.—E. Hirschsohn (*Pharm. Zeitung für Russland*).—Twenty to thirty drops of the balsam in question are covered with 1 to 2 c.c. of a solution of 1 part caustic soda in 5 parts alcohol (at 95 per cent), boiled up several times, and when cold mixed with twice its volume of ether. If oil is present the mixture is gelatinous.

Contributions to Forensic Chemistry.—W. Lenz.—The author collates procedures published by Dragendorff for a number of powerful agents. The detection in general is effected according to Dragendorff's general method. The acidulation of the mixture to be submitted to "shaking out" is always effected with dilute sulphuric acid, and alkylation with ammonia. The substances especially considered are (a) the esters of guaiacol, naphthol, cresol, &c., and (b) amidic compounds.

Experiments on the Atomic Weight of Cobalt.—H. Thiele.—Already inserted.

To this issue there is appended a very complete table for calculating the phosphoric acid in magnesium phosphate. The table gives the corresponding weights of P_2O_5 in grms. for all weights of $Mg_2P_2O_7$ from 0.0001 grm. to 0.4000 grm., the coefficient being 0.63964. The calculations have been collated by Dr. Götschke, of Brunswick.

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APPOINTMENT OF DEMONSTRATOR IN CHEMICAL DEPARTMENT.

The Council invite Applications on or before the 10TH SEPTEMBER, 1896, for the above appointment, vacant in consequence of the appointment of Dr. Boyd as Lecturer in Chemistry to the Hartley Institution, Southampton. The duties will commence on October 1st, 1896.

Particulars of the stipend, conditions, and duties will be sent on application to the undersigned, to whom all applications for the appointment should be sent.

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1919.

FOURTEENTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

THE Committee on Indexing Chemical Literature presents to the Chemical Section its Fourteenth Annual Report.

During the year ending August, 1896, there has been exhibited much activity in chemical bibliography and indexing; several valuable works have been completed and many important undertakings have been begun.

Works Published.

"A Dictionary of Chemical Solubilities." *Inorganic*. By Arthur Messenger Comey. New York and London, 1896. Pp. xx.—515. 8vo.

Professor Comey is to be complimented on the completion of the first part of his extensive undertaking, and chemists are to be congratulated on the publication in such good form of so important an aid to research. It is to be hoped that this volume will be so well received as to encourage the author to follow promptly with the organic section.

"Index to the Literature of the Detection and Estimation of Fusel Oil in Spirits." By W. D. Bigelow. *Journ. Amer. Chem. Soc.*, vol. xviii., No. 4, p. 397.

This was announced in our report for 1895.

"Bibliography of Embalming," in a Thesis entitled: "Embalming and Embalming Fluids," by Charles W. McCurdy (of the University of Idaho). *Post Graduate and Wooster Quarterly*, April, 1896.

A very full bibliography of this unique subject, which has its chemical aspects as well as its grave ones. It comprises about 500 entries, in several modern languages, arranged alphabetically by authors.

"References to Capillarity," by John Uri Lloyd. In his "Study in Pharmacy." Privately printed. Chicago, 1895—96. 8vo.

"Atomic Weights" form the subject of a brief bibliography (24 titles) accompanying an article on the same topic by Alexander Scott. *Science Progress*, vol. i., p. 542 (Aug., 1894).

"The Composition of Water." A short bibliography. By T. C. Warrington. *CHEM. NEWS*, vol. lxxiii., p. 137 *et seq.* (March, 1896).

"A Short List of Books on Chemistry." Selected and annotated by H. Carrington Bolton. *Scientific American Supplement*, O&A, 19, 1895.

"Bibliography as a Feature of the Chemical Curriculum." By H. Carrington Bolton. *Science*, O&A, 4, 1895.

"Review of American Chemical Research." Edited by Arthur A. Noyes. In the *Technology Quarterly*, issued by the Massachusetts Institute of Technology, Boston, Mass.

The first paper appeared in the number for April, 1895 (vol. viii., p. 90); the reviews consist of abstracts of papers in periodicals, grouped under the following heads:—General and Physical Chemistry, Inorganic, Organic, Technical, Sanitary, Agricultural, Vegetable, Metallurgical, Assaying, Geological, Mineralogical, Apparatus. Each abstract is signed by the abstractor.

* Advance proofs from the *Proceedings of the American Association for the Advancement of Science*, Buffalo Meeting, August, 1896. Communicated by H. Carrington Bolton.

This Review promises to be an important contribution to contemporary chemical science of America, and deserves to be well supported.

"Enumeration of Titles of Chemical Papers." This bibliography has been published monthly since May, 1894, in *Science Progress*, London. It embraces titles (without comments) in several European languages.

"Bibliography of Agricultural Chemistry (American)." The several publications of the scientific bureaus of the United States Government contain many valuable contributions to chemistry in its applications to agriculture and the arts, widely scattered in their pages, and it has been difficult to keep informed with reference to them. Thanks, however, to the excellent bibliographical work of the Office of Experiment Stations, U. S. Department of Agriculture, Washington, D.C., the chemical treatises published in the Bulletins of the State Institutions are made accessible; this is accomplished in the three publications here named:—*Experiment Station Record*, vol. iii., No. 12, July, 1892. *Bulletin*, No. 19 (1894), and *Bulletin*, No. 23 (1895). Organisation Lists of the Agricultural Experiment Stations, U. S. Department of Agriculture, Office of Experiment Stations.

These contain: "Lists of Station Publications," giving dates, bulletin-numbers, and titles of each bulletin, under each State, alphabetically arranged. For the agricultural chemist these bibliographical helps are too important to be overlooked.

The Committee also chronicles the publication of the following valuable aids to chemical research:—

"Synopsis of Current Electrical Literature during 1895." By Max Osterberg. New York (D. van Nostrand Co.), 1896. Pp. xiii.—143. 8vo.

This is a classified index with an index to authors, compiled from fifty-nine foreign and American periodicals; it is intended to be published annually.

"General-Register zu Ladenburg's Handwörterbuch der Chemie." Breslau, 1895. Pp. 160. 8vo.

"Bibliographie des travaux scientifiques" publié par les sociétés savantes de la France, dressés sous les auspices du ministère de l'instruction publique; par J. Deniker. Paris, 1895. 4to.

Reports of Progress.

The "Index to the Mineral Waters of the World," by Dr. Alfred Tuckerman, noticed in previous reports has been completed and accepted for publication by the Smithsonian Institution.

The manuscript of a new edition of the "Catalogue of Scientific and Technical Periodicals, 1865-1882," by Dr. H. Carrington Bolton, has been completed and is now going through the press. The new edition will be issued by the Smithsonian Institution as a volume of the Miscellaneous Collections. The bibliography includes chemical journals, and is brought down to the year 1895.

Dr. Bolton reports progress on a Supplement to his "Select Bibliography of Chemistry, 1492-1892," the printing of which is, however, postponed.

Professor James Lewis Howe reports the completion of the manuscript of an "Index to the Literature of Platinum and its Compounds"; this will be presented to the Chemical Section at the same session with this report.

Professor F. P. Venable has completed an "Index to the Literature of the Periodic Law." It will accompany his "Development of the Periodic Law," soon to be published by the Chemical Publishing Co., Easton, Pa.

Works in Preparation.

Dr. Alexis A. Julien has no less than three bibliographical works well advanced:—(1) "A Bibliography of Sand" (including chemical analysis, &c.).

(2) "A Bibliography of Pedesis, or the Brownian Movement."

(3) "A Bibliography of the Condensation of Gases on the Surface of Solids."

Dr. Arthur C. Langmuir is engaged on an "Index to the Literature of Zirconium."

Mr. George Wagner, of the University of Kansas, has undertaken an "Index to the Literature of Oxygen," on a large scale. In this work he will have the counsel of Professor Albert B. Prescott.

Dr. C. H. Joët has the manuscript of an "Index to the Literature of Thorium" well advanced towards completion.

Professor Rudolf A. Witthaus has compiled a "Bibliography of Forensic Toxicology," which will appear in Vol. IV. of Witthaus and Becker's "Medical Jurisprudence," New York, 1896.

The *Journal of the Society of Chemical Industry* announces a Collective Index for the whole series, 1881-1895. This is to be ready in 1896, and will form a volume of about 500 pages quarto.

Attention is called to a plan for facilitating bibliographical researches, adopted by the American Pharmaceutical Association. The Research Committee of this Association employs a Reference Reader whose duty it is to supply original literature to investigators working in the Committee and with it. A list of the chief serials and a few encyclopædic works is placed in the hands of those who apply for the services of the Reader. Transcripts, abstracts, and translations are supplied. The service is chiefly for literature beyond the smaller libraries, and is under the direction of the Chairman of the Committee.

Perhaps a similar scheme might be organised within the American Association for the Advancement of Science.

In conclusion, the Committee on Indexing Chemical Literature desires to state to those not acquainted with the announcements made in the preceding annual reports that it labours to foster individual undertakings in chemical bibliography, to prevent futile duplication of work, to record in these reports completed bibliographies and new enterprises, as well as to chronicle progress in bibliography in lines bordering on chemistry. Suggestions as to topics, methods, channels of publication, &c., will be cordially furnished by the Committee. Address correspondence to the Chairman, at Cosmos Club, Washington, D.C.

Committee:—

H. CARRINGTON BOLTON, Chairman,
F. W. CLARKE,
A. R. LEEDS,
A. B. PRESCOTT,
ALFRED TUCKERMAN,
H. W. WILEY.

The Chemical Laboratory of Wiesbaden.—In the Summer Term, 1896, there were 63 students on the books. Of these, 39 were from Germany, 12 from Russia, 4 from England, 2 from Holland, 2 from North America, 1 from Austro-Hungary, 1 from Switzerland, 1 from Italy, and 1 from Spain. The assistants in the instruction laboratory were three in number, in the private laboratory twenty-one, and in the Versuchsstation two. Besides the director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged, as teachers in the establishment, Prof. Dr. H. Fresenius, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, Dr. W. Lenz, Dr. L. Grünhut, and Architect T. Brahm. The next Winter Term begins on the 15th of October. In the different departments of the Laboratory and in the Versuchsstation, besides the scientific researches, a great number of analyses were undertaken on behalf of manufacture, trade, mining, agriculture, and hygiene.

DETERMINATION OF IRON OXIDE AND ALUMINA IN PHOSPHATE ROCK BY THE AMMONIUM ACETATE METHOD.

By THOMAS S. GLADDING.

THE oldest method of separating alumina and iron phosphates from lime phosphate is, probably, the ammonium acetate method. This has been severely criticised, and just at present seems to be under condemnation. The following investigation has convinced the writer that, when properly carried out, not only does the method give an accurate separation of iron and alumina from lime phosphate, but also gives a neutral phosphate of uniform composition from which the iron oxide and alumina present may be accurately estimated.

In brief, the method used is this:—If a weakly acid solution of phosphates of iron and alumina, together with a large amount of calcium phosphate, be slowly poured into a strong solution of ammonium acetate made acid with acetic acid, the iron and alumina are precipitated as phosphates, upon digestion for a short time at a gentle heat. This precipitate, however, contains more or less calcium phosphate, which is removed by several re-precipitations. I shall demonstrate by experiment:—

First. That upon continued re-precipitations of iron and alumina as phosphates in this manner, there is no appreciable diminution of the quantity of either finally obtained, provided there always be a large excess of phosphoric acid present.

A standard solution was made by dissolving 20 grms. of ammonia alum (C. P.) in distilled water. This was slightly acidified with hydrochloric acid, in order to prevent the alumina from separating on standing, and diluted to 1 litre. This solution, upon being standardised, was found to contain the theoretical amount of alumina, that is—

Ten c.c. = 0.0225 gm. Al_2O_3 .

One precipitation, in the manner described above, of the alumina in 10 c.c. gave—

	$\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$, found.	Al_2O_3 .
1	0.0545	0.0228
2	0.0549	0.0229
3	0.0546	0.0228
4	0.0540	0.0226
5	0.0545	0.0228

Three successive precipitations, in which 1 gm. of ammonium phosphate was added before each precipitation, gave—

	$\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$.	Al_2O_3 .
1	0.0550	0.0230
2	0.0547	0.0229
3	0.0544	0.0227

Five successive precipitations were also tried under the same conditions, with the following results:—

	$\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$.	Al_2O_3 .
1	0.0536	0.0224
2	0.0530	0.0222

When, however, the excess of phosphoric acid was omitted before the re-precipitations, there was a loss of alumina.

An iron solution was made by dissolving C. P. iron wire in hydrochloric acid and oxidising it with nitric acid. When carefully standardised it was found that—

Ten c.c. = 0.0296 Fe_2O_3 .

Three successive precipitations, adding 1 gm. ammonium phosphate before each, gave—

	$\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$.	Fe_2O_3 .
1	0.0545	0.0289
2	0.0550	0.0291
3	0.0548	0.0290

Five successive precipitations, in the same way, gave—

	$\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$.	Fe_2O_3
1	0'0550	0'0291
2	0'0560	0'0297

Second. That upon three successive precipitations in the presence of a large amount of calcium phosphate, as is the case in the analysis of rock phosphate, the precipitate of the phosphates of iron and alumina is sufficiently pure to be taken as such. Of the standard solutions, 5 c.c. of each would together give a precipitate of combined phosphates about equal to that usually found in 1 grm. of phosphate rock. The mixture so analysed was made up as follows:—

Five c.c. alumina solution = 0'01125 Al_2O_3 .

Five c.c. iron solution = 0'01480 Fe_2O_3 .

0'7000 grm. calcium phosphate.

This was given three precipitations, the excess of phosphoric acid being supplied before the second and third precipitations.

	Phosphates obtained.	Al_2O_3 obtained.	Fe_2O_3 obtained.
1	0'0552	0'0115	0'0146
2	0'0540	0'0110	0'0146
3	0'0537	0'0109	0'0146
4	0'0536	0'0109	0'0146

The iron oxide was determined by volumetric method in the ignited precipitate, and the alumina by subsequent calculation.

In addition, 20 c.c. alumina solution, containing 0'0450 grm. Al_2O_3 , together with 0'700 grm. calcium phosphate, were given three successive precipitations in the same way, with the following results:—

	$\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ obtained. Grm.	Al_2O_3 obtained. Grm.
1	0'1092	0'0456
2	0'1074	0'0449

In order to prove that the aluminum phosphate precipitated was the normal phosphate, the ignited precipitates were fused, and the phosphoric acid in them estimated.

	$\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$.	P_2O_5 obtained.	Al_2O_3 by diff.	Al_2O_3 by calc.
1	0'0538	0'0313	0'0225	0'0225
2	0'0533	0'0312	0'0221	0'0223

The phosphate of alumina is multiplied by the factor 0'418 to obtain the alumina.

Therefore, in determining iron oxide and alumina in phosphate rocks, proceed as follows:—

Four grms. of the finely-ground sample, previously freed by a magnet from any metallic iron derived from the iron mortar used in grinding the sample, are digested for half an hour, at a temperature just below the boiling-point, with about 30 c.c. dilute hydrochloric acid (1—1). This will prevent the solution of any pyrites, if present. Filter and wash thoroughly into a 200 c.c. flask, add a little nitric acid, and boil to oxidise the iron; cool, and fill to mark with water. Take two portions, 50 c.c. = 1 grm., 25 c.c. = $\frac{1}{2}$ grm., and proceed with each as follows:—

Almost neutralise the solutions with strong ammonium hydroxide until the precipitate formed dissolves with difficulty, and thoroughly cool by placing the beaker in a dish of cold water. The neutralisation is then completed by carefully adding dilute ammonium hydroxide until the precipitate remains permanent, then just dissolve by adding dilute hydrochloric acid, drop by drop, stirring well. Have ready in another beaker a mixture of 15 c.c. of a strong solution of ammonium acetate (made by neutralising 30 per cent acetic acid with strong ammonium hydroxide) and 5 c.c. of acetic acid. Carefully pour the cold faintly acid solution of phosphates in a fine stream into this mixture, stirring all the while. Digest at 60° C. from one-half hour to one hour, until the supernatant liquid is clear and the flocculent precipitate is well settled to the bottom.

Filter and wash the precipitate once with a 10 per cent ammonium acetate solution, merely rinsing out the beaker in which the precipitation was made. Dissolve the precipitate from the paper into the same beaker with a few c.c. of hot dilute hydrochloric acid (1—4). Use as little acid as possible, in order to keep the bulk of the solution small. Add 1 grm. of ammonium phosphate, neutralise with ammonium hydroxide, and add hydrochloric acid until the precipitate just dissolves as before, and pour into a mixture of 15 c.c. ammonium acetate solution and 5 c.c. acetic acid. Digest at 60° C. for one-half to one hour and filter, and wash once with the 10 per cent ammonium acetate solution. Re-dissolve and repeat the precipitation, being careful to again add 1 grm. of ammonium phosphate to the solution, in order that there be a sufficient excess of phosphorus pentoxide to precipitate all the alumina as a neutral phosphate. Wash the precipitate three times with dilute ammonium acetate solution.

Take the filter, while wet, from the funnel, and ignite in a tared platinum capsule, using a very low flame until the filter-paper is thoroughly charred. The heat is increased gradually until the paper is completely consumed, and finally the blast-lamp is used for a minute. Weigh as combined phosphates of iron and alumina. The iron is determined volumetrically in the solution of the weighed precipitates. The iron oxide present in the rock is also determined separately by volumetric process, preferably the bichromate method, in a solution of 5 grms. of the rock in dilute hydrochloric acid (1—1), reducing all iron to protoxide and titrating with bichromate.

The ignited precipitate from one of the duplicate precipitations may, if desired, be dissolved and subjected to a fourth precipitation, and the filtrate tested for lime by adding ammonium oxalate and heating. My thanks are due to our assistant, Thomas Brown, jun., for valuable aid in the above analytical determinations.—*Journal of the American Chemical Society*, vol. xviii., No. 8.

ON SOME NEW SOUTH WALES AND OTHER MINERALS.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

Antimonite.—Queensland.

A HARD splintery variety, breaking with a conchoidal fracture with somewhat hackly surfaces; noticeable as containing silica and barytes in thin veins or joints.

Analysis.

Antimony	64'47
Sulphur	26'59
Iron	1'00
Silica	3'41
Barium sulphate	2'63
Undetermined and loss	1'90

100'00

The above is the mean of two analyses. Sp. gr. 4'43.

Apatite, Plumbiferous.—Calcium fluo-phosphate. Broken Hill.

Some specimens of apatite containing lead were forwarded to me by Mr. S. Harris, from Block 14 Mine for examination.

The apatite is in the form of small grey imperfect crystals (some, however, are symmetrical hexagonal prisms closed by the pyramid and terminal pinacoids), about one-sixteenth inch long, in cavities in a matrix of dark blue-black honey-combed crystalline zinciferous galena; the freshly fractured apatite has somewhat the lustre and

* Read before the Royal Society of N. S. Wales.

appearance of pyromorphite. It is probable that part of the calcium phosphate of the apatite is replaced by the isomorphous lead phosphate.

The crystals of apatite were separated as carefully as possible from the galena, but this could not be done completely, as small crystals of galena are seen within the apatite crystals, *i.e.*, when sliced and examined under the microscope.

Mr. Harris states that pyromorphite was met with in the shallower parts of the same portion of the mine in considerable quantities. He found 3.9 per cent of fluorine, 0.5 per cent manganese monoxide, and 36.25 per cent of phosphorus pentoxide, but as all the specimens I examined showed enclosed lead sulphide, I do not quote his amounts of lead and lime; the proportions of phosphoric oxide and fluorine indicate that the mineral answers to the general formula of $3\text{Ca}_2\text{P}_2\text{O}_8\cdot\text{CaF}_2$, in which part of the Ca is probably replaced by Pb.

Barklyite.—Two Mile Flat, Mudgee, N.S.W.

Collected by the late Prof. A. M. Thomson, Sydney University.

The specimens were in small well-rolled pebbles, not more than $\frac{1}{2}$ inch long. Most are of a kind of dull magenta colour and usually show one or two light streaks or veins; in others, the colour might be referred to that of lean beef. Hardness about 8.5, *i.e.*, less than 9. Sp. gr. 3.738 at 18.5° C.

The mineral is tough, and the fracture granular and of a pink tint; the powder is also of a pale pink tint. Before the blowpipe it darkens a little and returns to its former colour on cooling. After ignition it is a little more opaque, probably due to slight disintegration. When strongly heated it becomes brilliantly luminous and gives a blue colour with cobalt nitrate. Large quantities give the chromium reaction with microcosmic salt and borax beads. The precipitate of $\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$, fused with NaKCO_3 gave the manganese reaction in one case but not in others.

No full description of this mineral appears to have been published; the name barklyite was given to it by Mr. Geo. Milner Stephen, F.G.S., after the then Governor of Victoria. In a catalogue of his collection, and in a lecture, he refers to them as violet rubies, or barklyite, from the Ovens district in Victoria (*Trans. Roy. Soc. Vict.*, 1865, p. 70). Apparently, too, it has never been met with in any quantity, and the variety does not appear to be sufficiently distinct to warrant a special name.

It consists principally of alumina (Al_2O_3), but the analysis in hand is not yet completed.

Chrysocolla.—Hydrous Copper Silicate. Broken Hill, N.S.W.

As incrustations and stalactitic forms, with mammillated surfaces, of a sky blue and green colour. Vitreous lustre in parts; conchoidal fracture; hardness, 4; streak, pale blue. Effervesces slightly on warming with HCl, from the presence of a little copper carbonate. Before the blowpipe it darkens and breaks up slowly with decrepitation. In tube it gives off much water and a nitrogenous odour. Soluble in HCl and HNO_3 with a residue of silica.

Beryl.—Vegetable Creek, New England, N.S.W.

Described in a paper read before the Royal Society of New South Wales, December 2, 1891. Sp. gr. 2.80; hardness, 7.5.

Analysis.				
Silica	67.4			
Alumina	18.5			
Beryllia	12.9			
Iron sesquioxide	0.6			
Lime	traces			
	99.4			

Crocoisite.—Dundas, Tasmania.

In brilliant crystals of a deep orange-red colour, about $\frac{1}{2}$ inch long, seated on a mangano-ferruginous matrix. The Dundas mines have yielded some fine groups of crocoisite crystals, with the prisms several inches long; associated with cerussite, galena, and occasionally angle-site and other lead minerals. Hardness, 2.5; sp. gr. 5.92.

Analysis.

Lead monoxide	66.86
Chromium trioxide	30.99
Iron sesquioxide	1.02
	98.87

Which corresponds with the formula PbCrO_4 .

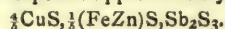
Fahlerz.—Wiseman's Creek, *via* Brewongle, N.S.W.

Occurs in quartz veins. Collected in September, 1888. No crystals were obtained.

Analysis.

Copper	33.004
Lead	0.630
Iron	2.844
Zinc	3.693
Antimony	34.620
Sulphur	25.207
Nickel	trace
Cobalt	trace
	99.998

The above corresponds approximately to—



Some silica was obtained in the analysis, but this was deducted and an allowance made for it in the calculation, as it obviously belonged to the matrix.

A special examination was made for gold and silver on a larger quantity, when 31 ozs. 17 dwts. 0 grs. of silver, and 2 ozs. 13 dwts. 8 grs. of gold per ton were found.

Ilmenite.—Cloncurry River, Queensland.

Black, with traces of crystal planes, breaks with well-marked metallic lustre.

Analysis.

Titanium dioxide, TiO_2	49.85
Silicon	1.01
Iron monoxide, FeO	35.70
Iron sesquioxide, Fe_2O_3	13.22

99.78

Manganese and magnesium are usually met with, but they and other metals, although specially sought for, were not found in this specimen. Dana gives the following extremes:—

TiO_2	= 59.20 to 3.55 per cent
FeO	= 46.53 to 3.26 "
Fe_2O_3	= 93.63 to 1.20 "

Zinciferous Galena.

This mineral was sent to me from Broken Hill as clausenthalite, the selenide of lead. Before the blowpipe it yielded the reactions lead, zinc, and sulphur, with a little arsenic, but I could not get any reaction for selenium. Decrepitates strongly. It appears to occur in nodular masses.

The mineral in certain lights has a dull grey colour and scoriaceous appearance, but in other positions the light is reflected from it brilliantly with a bluish grey metallic lustre; this is due to the fact that the surface is covered with minute cubical crystals, which have their planes more or less parallel, although at different levels; my specimens only exposed about 2 square inches, but I think it would be found to extend over larger surfaces. The effect is something like that of "shot" silk.

Under a 1 inch objective the cubical character of the crystals are clearly recognisable, so also are the well-marked cubical cleavage planes, which have a strong metallic lustre. The mineral appears to be homogeneous, and no separate portions of blende were detected in it, so that the two sulphides seem to have been deposited together; thin films of arborescent copper pyrites occur on some of the surfaces, and within crevices. Sp. gr. at 18° 6.72. It is slightly harder than galena.

The nodules only contain a little zinc; but they have not yet been analysed; on assay they proved to be very rich in gold, and gave me 5 ozs. 17 dwts. 4 grs. per ton, and 0 oz. 19 dwts. 4 grs. of silver per ton; lead minerals are usually richer in silver than in gold.

The vein stuff gave—

	Analysis.		
	I.	II.	III.
Insoluble	3.16	3.47	—
Lead	60.20	—	61.014
Zinc	15.50	14.85	—
Sulphur	18.94	—	—
Iron	2.62	—	—
Copper	0.205	—	—
Arsenic	traces	—	—
Antimony	traces	—	—
100.625			

The proportion is about 3PbS, 2½ZnS.

It seems to be related to the minerals huascolite and kilmacooite (Dana's "System of Mineralogy," 1892, p. 51), but with fairly well marked differences. I do not, however, think it need be named; the term zinciferous galena describes it accurately without adding to the already excessive list of so-called new species of minerals.

Limestone with Cone-in-cone Structure.—Pitcon, N.S.W.

Evidently very impure, of a brown colour, and argillaceous appearance. An analysis of this was made in 1876, and forwarded to the Mineralogical Society, but lost in transit.

Composition.		
Portion soluble in HCl:—		
Water		2.10
Carbon dioxide, CO ₂		30.01
Silica, SiO ₂		1.63
Iron sesquioxide, Fe ₂ O ₃		4.35
Manganese oxide, MnO		0.52
Lime, CaO		38.19
Soda, Na ₂ O		1.70
Portion insoluble in HCl		22.21
100.71		

The amount of calcium carbonate being 68.20. The portion insoluble in hydrochloric acid was not further examined.

The specimen was from a layer about three inches thick; the cones are fairly regular in size and shape, and run right through the deposit in vertical columns, like piles of small closely packed conical paper sugar-bags; the average diameter being about half an inch, and the length perhaps a little more, the angle of the cone being between fifty and sixty degrees, and incipient crystallisation is visible in parts. The upper surface of the deposit presents pits with thickened edges over some of the columns of cones.

Mr. A. J. Sach, F.C.S., published an account of this deposit (with an analysis) in the "Report of the Australasian Association for the Advancement of Science," Hobart Session, 1892, p. 328.

Molybdenite.

This was described in "Note No. 6," read before this Society, December 2, 1891, as occurring in large crystals, 3×3½×5½ inches long, from the Eleanor Mine, Kingsgate, near Glen Innes, N.S.W.

Composition.

	I.	II.
Molybdenum	57.31	58.66
Sulphur	42.00	41.23
Iron	1.50	0.39
100.81		100.28

Another specimen yielded about 6 per cent of manganese oxide; but this was probably mechanically enclosed between the plates of molybdenite. Sp. gr. 4.6.

Proustite.—Silver Sulpharsenide.

Mr. Edgar Hall, F.C.S., sent me, in August last, some specimens from his United Mine at Rivertree, in which he had found some minute red crystals. I have examined the crystals, and agree with him in regarding them as proustite. They are quite microscopic, and it is difficult to examine them and still more to separate them from the matrix.

Mr. Hall states that they occur in a narrow vein, about half an inch thick on the hanging wall, and that they have been met with at 70 feet, 120 feet, and 180 feet levels; in fact, all the way down so far. The lode is a contact one, between a dyke of quartz diorite and the massive granite of the country. The fissure is about 8 feet wide at the 120-foot level, of which about 4 feet is quartz carrying argentiferous minerals; the yield of silver is found to be much greater where the proustite crystals are present.

The crystals are on a bluish quartz, containing mispickel; they are of a full red colour, translucent, with vitreous lustre, and about one-tenth to one-fifth m.m. in length. I was able to obtain the reactions for arsenic, sulphur, and silver, but no attempt was made to make a quantitative analysis, as it was only with difficulty that a few hundredths of a grain were obtainable.

Proustite is reported by Mr. C. Marsh ("Geology of the Broken Hill Lode, &c.," by J. B. Jaquet, p. 90, Sydney, 1894) to occur also at Broken Hill.

Scheelite.—Calcium Tungstate, CaWO₄.

Lady Hopetoun Mine, Glen Innes, N.S.W.

Massive, coarsely crystalline, of a pale brownish stone colour. Hardness, 5; sp. gr. 5.93, another portion 5.3 only.

A fairly pure calcium tungstate, containing a little water, 2.23 per cent of silica, 1.52 per cent of iron sesquioxide, and a trace of manganese.

Tinstone Crystals.—Elsmore Mine, Inverell, N.S.W.

In stout pyramids, usually about half an inch through, but some of them are much larger. Very slightly water-worn at the edge, otherwise the crystals have the faces of the pyramid well developed and of a high metallic lustre. Yielded a white powder. Sp. gr. 6.68; hardness, 6.5.

Analysis.

Tin oxide, SnO ₂	94.60
Silica, SiO ₂	2.00
Iron sesquioxide, Fe ₂ O ₃	1.67
Manganese oxide, MnO	0.25
Tungstic acid, WO ₃	0.06
98.58	

Another specimen from the same locality, but water-worn, was found to be harder, = 7, with a sp. gr. of 6.54. The powder of this was brown.

Analysis.

Tin oxide, SnO ₂	92.52
Silica, SiO ₂	1.68
Oxide of manganese, MnO	0.98
Iron sesquioxide, Fe ₂ O ₃	3.21
Tungstic acid, WO ₃	0.36
98.75	

The loss of 1.25 on this and 1.42 on the previous specimen may indicate the presence of some of the rarer elements not specially sought for, and that the specimens are worthy of further examination.

Topaz.—Shoalhaven District.

In the form of short columnar prisms, the terminal pyramidal planes not well developed, seated on granite. Of a greyish tint, more or less opaque, but translucent in parts.

Most of the crystals were about one-fifth to one-fourth inch in diameter, and about $\frac{1}{4}$ inch long, closely packed together so as to form a solid layer of topaz next to the supporting rock. The crystals are brittle, some of the faces are slightly rough, as if etched. Hardness, 7.5 only; sp. gr., 3.56.

Before the blowpipe it decrepitates, darkens, but becomes nearly colourless again on cooling. Gives off a little water when heated in tube.

Analysis.

Silica	28.19
Alumina	62.66
Fluorine	14.01
Water at 100°	1.21

106.07

The above are the mean of the results of two closely agreeing analyses. The oxygen equivalent to the fluorine must be allowed for in the above analysis.

In the foregoing paper I was assisted by Mr. A. O. Black, a student in the Chemical Laboratory, who, under my direction, made several of the analyses; Mr. C. Walker, another student, analysed the ilmenite; Mr. J. A. Schofield, A.R.S.M., F.C.S., Demonstrator, the zinciferous galena; and Mr. J. M. Petrie, Junior Demonstrator, the fahlerz.

THE SEPARATION OF TRIMETHYLAMINE FROM AMMONIA.*

By HERMANN FLECK.

THE quantitative estimation of trimethylamine in presence of ammonia is, I believe, not mentioned in the literature, although a number of publications have appeared in which the detection of trimethylamine, in presence of ammonia, by means of the different solubilities of their hydrochlorides in absolute alcohol, has been successfully carried out.

Dessaignes (*Ann. Chem.*, Liebig, lxxx., 106) prepared and analysed with good results the platinum double salt of trimethylamine, by conducting the mixture of ammonia and trimethylamine vapours into hydrochloric acid, evaporating to dryness, extracting with absolute alcohol, precipitating with platinic chloride, and re-crystallising the precipitate formed several times from hot water.

Wicke (*Ann. Chem.*, Liebig, xci., 121) adopts the same method, using, however, alcohol-ether extract.

Winkles (*Ann. Chem.*, Liebig, xciii., 321), in using this method, further states that while ammonium chloride is soluble to some extent in absolute alcohol, it is rendered totally insoluble by the presence of salts of such bases as trimethylamine.

Eisenberg (*Ber. d. Chem. Ges.*, 1880, 1669), by a similar procedure, obtained the platinum double salt in crystals of great purity and perfection.

The success in each case is undoubtedly due to the fact that large quantities of hydrochlorides were used. Winkles (*loc. cit.*), for example, employed the hydrochlorides obtained from 26 gallons of herring brine. Further the mixtures were very rich in trimethylamine.

This method applied to a substance containing a low percentage of the latter yielded results which clearly show that trimethylamine hydrochloride does not render ammonium chloride insoluble in absolute alcohol, and further does not serve as a good means of qualitative, much less of quantitative, separation. A portion of the mixture containing trimethylamine and ammonia was saturated with hydrochloric acid, evaporated to dryness, and extracted several times with portions of several times the volume of boiling absolute alcohol. The alcoholic extract evaporated to dryness gave 18 per cent of supposed trimethylamine hydrochloride. To identify the latter, the residue was taken up with alcohol and platinic chloride added. The precipitate formed was re-dissolved in boiling water, and the different fractional crystallisations, consisting of octahedra, analysed.

	Pt found.	Required for
First crystallisation	43.6	(NH ₄ Cl) ₂ PtCl ₄ , 43.84
Last	39.5	Corresponding to a mixture of
		2 [(NH ₄ Cl) ₂ PtCl ₄] +
		3 [N(CH ₃) ₃ .HCl] ₂ PtCl ₄ ,
		which require 39.4 p. c. Pt.

Intermediate crystallisations gave intermediate, gradually decreasing results, showing that the isomorphous forms of the two salts crystallised together.

Duvillier, Buisine (*Ann. Chem.*, Liebig (5), xxiii., 299) extract the mixed sulphates to prepare pure trimethylamine from the technical product. The suggestion led to the use of the following method, which yielded satisfactory results.

The mixed hydrochlorides are repeatedly extracted with portions of five or six times the volume of boiling absolute alcohol, and the solvent distilled off in a three-quarter litre distilling bulb. An excess of caustic soda is added to the residue, and the gases formed on boiling driven over into a large quantity of water. Litmus is added, followed by the exact quantity of dilute sulphuric acid required to neutralise. The liquid is evaporated to dryness and extracted with 1 litre cold absolute alcohol in which trimethylamine sulphate dissolves, leaving ammonium sulphate undissolved. The alcohol is distilled off, the residue transferred to a weighed dish, dried, and weighed. In this manner 32.910 grms. of the carefully-dried mixed chlorides gave 2.16 grms. trimethylamine sulphate, corresponding to 2.21 grms. hydrochloride, or 6.71 per cent.

That the extraction was complete is evident from the total absence of the fishy odour when the extracted residues are treated with alkali. That the extracted material is pure is shown by the following analyses of the octahedral crystals of the platinum double salt prepared from the trimethylamine sulphate:—

	Per cent Pt.	Required for [N(CH ₃) ₃ .HCl] ₂ PtCl ₄ , Per cent Pt.
I. 0.0983 grm. gave ..	36.92	—
II. 0.3017	37.12	36.93

VOLUMETRIC ESTIMATION OF HYDROXIDES AND CARBONATES; AS ALSO OF THE MONO- AND BICARBONATES OF THE ALKALIS, ALKALINE EARTHS, AND MAGNESIA.

By C. KIPPENBERGER.

THE author has used a series of colouring-matters as indicators. In general they may be used along with methyl-orange, which is not sensitive to carbonic acid, thus frequently simplifying the operation. The change of colour of these indicators is shown in the accompanying table.

* Contribution from John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, vol. xviii., No. 8, August, 1896.

By—	Hematoxyline.	Gallein.	Alkanin.	Gentiana blue.	Blue de Lyon.	Poirrier's Blue.
Hydroxide	Blue	Blue	Blue	Deep blue	Red	Red
Alkali .. { Carbon.	Red	{ Blue, turning } red	Blue	Red	Red	{ In strong solutions red, turning blue.
		Red	Red	Blue	Blue	Blue
Alk. earths { Carbon.	Red	Red	Red	Blue	Blue	Blue
		Red	Red	Blue	Blue	Blue
Magnesium { Carbon.	Blue	Blue	Blue	} Blue {	Red	} Blue
	Red	Red	Red		Blue	

Hematoxyline was tried with magnesium carbonate and mixtures of alkaline hydroxide and carbonate. In the former case the results were too low by $\frac{1}{3}$; in the second there is formed, on the addition of the indicator, a dark mixed colour which after the hydroxide has been converted into a salt changes to the red colouration characteristic of the alkaline carbonate.

Gallein certainly colours a mixture of alkaline hydroxide and carbonate blue; but on the addition of an acid the red colouration does not appear when the hydroxide is converted into a neutral salt and the carbonate into bicarbonate, but earlier. The author refers this phenomenon to the formation of sesqui-carbonate, which effects the change. When gallein is used the acid must not be too strong, centinormal sulphuric acid being the most suitable. Stronger acid occasions a development of carbonic acid, which has a disturbing effect. The results, however, do not agree very well even on the use of this dilute acid.

Phenolphthalein, alkanin, and blue de Lyon are not sensitive to sesquicarbonates, and are therefore more suitable than hematoxyline and gallein for the above-mentioned substances when jointly present. Gentiana blue cannot well be used along with decinormal and centinormal liquids.

Poirrier's blue (C₄B) yields, according to Engel and Ville, a blue colour with alkaline carbonates and a red with hydroxides. Kippenberger observed that in concentrated solutions carbonates also give a red colour, and the blue colouration makes its appearance when the solution has the strength of a normal liquid. Sesquicarbonates and bicarbonates show a rather lighter blue colour. Water is not without influence on the colour, and liquids which are more dilute than decinormal cannot be titrated. The author observed, as had been previously done by Lunge, that the results obtained with Poirrier's blue are always too low.

Sulphindigotic acid, which has been also recommended by Engel and Ville, gives no accurate results.

Flavescin, recommended by Lux (*Zeit. Anal. Chemie*, xix., 459) gives very useful results. The author, however, does not use this indicator alone, but along with methyl-orange, like the foregoing. This procedure has the advantage that, after the conversion of the hydroxide into neutral salts, and of the carbonate into bicarbonate, it is possible to titrate to the conclusion in the cold, whilst, according to Lux, the liquid is boiled after the addition of more acid, and after the expulsion of the carbonic acid it is titrated back with lye until yellowness.

The calculation, on employment of the titration-method, is simple. At first the hydroxide and the half of the carbonate is neutralised, and then the second half of the carbonate is titrated, using methyl-orange as an indicator. If mono- and bicarbonate are jointly present, the half of the former is determined in the first phase, and then the other half of the former and the bicarbonate are determined in the second phase.

Dissolved hydroxides of the alkaline earths along with alkaline hydroxides can be determined by first effecting a general determination, and then, in another portion of the liquid, after precipitation of the hydroxides of the alkaline earths with a standard solution of carbonate, the hydroxide and carbonate are then determined in an aliquot portion, as above described. Magnesium carbonate in

presence of alkali carbonate, is determined in an analogous manner, when we add (whilst heating) alkaline hydroxide and titrate magnesium carbonate with the use of hematoxyline, where, however, only two-thirds of the whole are determined.—*Zeitschrift für Analyt. Chemie*, xxxv., Part 3, p. 334.

ON A DISTINCTIVE CHARACTER OF ORDINARY MAGENTA AND OF ACID MAGENTA S. ON SCHIFF'S REACTION.

By P. CAZENEUVE.

MAGENTA or rosaniline hydrochlorate, and more generally all the salts of this base, possess the property, if decolourised with sulphurous acid, of giving—in contact with alcohol mixed with ordinary aldehyd or its kindred homologues—a violet colouration differing from the shade of the original magenta. The aromatic aldehyds, likewise, give the re-colouration.

A very small quantity of aldehyd sets up the reaction (Schiff). We may proceed in the following manner:—

Some c.c. of an aqueous solution of a salt of rosaniline, at 1/1000, are decolourised with a solution of sulphurous acid. The addition of alcohol, mixed with formic or with ethylic aldehyd, likewise develops the violet colouration.

Magenta S, a commercial acid magenta, which is in reality a sodium rosaniline di- or trisulpho-conjugated, if similarly treated gives nothing,—that is, the solution, if decolourised with sulphurous acid, does not turn to a violet on the addition of alcohol charged with aldehyd.

According to the proportion of alcohol added the decolourised solution resumes a rose tint, which is the original colour much diluted. It must otherwise be noted that the richer the alcohol in aldehyd the less does this light rose tint appear.

The addition of hydrochloric acid does not modify the negative result obtained with magenta, but it accentuates the colouration given by the salts of ordinary rosaniline.

These two magentas, therefore, behave in a very different manner with alcohol charged with aldehyds. This fact merits the more notice as some authors assert that ordinary magenta and magenta S behave in an identical manner with reagents.

This assertion is already erroneous, because we know that magenta S, if heated with an alkali, does not enter into amylic alcohol like ordinary magenta, and that it resists the oxidising action of manganese peroxide, as I have already shown for its detection in wines.

To return to the action of aldehyds:—If we wish to proceed methodically, and prepare the conditions for this differential reaction in a course of lectures on colouring-matters, we may prepare the following solutions, the one made with an ordinary salt of rosaniline and the other with magenta S.

Water	200 C.C.
Solution of magenta at 1/1000	30 "
Sodium bisulphite at sp. gr. 1.288	40 "
Sulphuric acid at sp. gr. 1.767	3 "

The addition of 4 c.c. of alcohol at 50 p.c. containing formic or ethylic aldehyd serves to distinguish the two solutions to the eyes of the pupils.

In a recent note on Schiff's reaction, M. Urbain sees, in this re-colouration of aldehyds of magenta which had been decolourised by sulphurous acid, the sign of the formation of condensation-products of the aldehyds and rosaniline, compounds which sulphurous acid does not decolourise.

This is only an hypothesis which requires to be proved by the isolation and the analysis of the colour formed.

In all cases, if this hypothesis is confirmed, the inaptitude of sulpho-conjugated rosaniline to become coloured in presence of the aldehyds leads us to think that the fixation of the aldehyds on the rosaniline molecule takes place at the same point of the nucleus where the sulpho-conjugation is effected.—*Bulletin de la Soc. Chimique de Paris*, Series 3, vol. xv.—xvi., p. 723.

THE INTRODUCTION OF STANDARD METHODS OF ANALYSIS.*

By the Baron HANNS JÜPTNER von JONSTORFF
(Neuberg, Austria).

(Continued from p. 102).

4. *Errors in the Operations.*—These include the unavoidable losses in the analysis, the action which results from the glass and porcelain vessels being attached, the variations in the ash contents of the filters used, &c. In this connection some of the numerous researches relating to these points may be referred to. According to R. Cowper (*Journal of the Chemical Society*, 1882, p. 254), when the following solutions, in quantities of 100 c.c., are heated for six days in glass vessels to 100° C., the following amounts of glass are dissolved:—

Reagent.	Glass dissolved in 100 c.c. Grm.	
Water	0'0080	0'0100
Sulphuretted hydrogen water ..	0'0125	0'0087
Dilute ammonium sulphide (prepared from 0'982 sp. gr. ammonia)	0'0496	0'0525
Concentrated ammonium sulphide (prepared from 0'88 sp. gr. ammonia)	0'0340	0'0472
Ammonia of 0'982 sp. gr. ..	0'0258	0'0425
Conc. ammonia, 0'88 sp. gr. ..	0'0075	0'0077

* Read before the Iron and Steel Institute.

R. Weber and Sauer (*Zeit. f. Ang. Chemie*, 1891, p. 662; *Ber. Deut. Chem. Ges.*, vol. xxv., pp. 70 and 1814) boiled various solvents in 100 c.c. flasks, made of different kinds of glass, replacing constantly the liquid boiled away, and obtained the results shown in the accompanying table.

Porcelain vessels are, as a rule, much less attacked. Thus R. Fresenius found that when the solvents named were boiled in Berlin porcelain dishes, the quantities dissolved, expressed in per cent of the solvents, were as follows:—

Solvent.	Quantity dissolved.	
Water	0'0005	
Pure hydrochloric acid	0'0053	0'0047
Ammonium chloride solution of 10 per cent strength	0'0393	
Crystallised sodium carbonate solution of 10 per cent strength	0'0243	

Unfortunately other firms place upon the market porcelain dishes which are very considerably attacked even by concentrated hydrochloric acid.

5. *Errors in the analytical methods* belong to the most important causes of differences in analytical results. They are so numerous and various that it must suffice to mention a few examples.

To these belong the incomplete oxidation of carbon in its determination with the aid of chromic acid and sulphuric acid; leaving out of consideration the various forms of the carbon in the Eggertz colorimetric method for the determination of carbon; the sulphur losses, which in all methods for the determination of sulphur that depend on the evolution of sulphuretted hydrogen, result from a portion of the sulphur remaining in the insoluble residue: the error in the manganese assay with lead peroxide due to the ready decomposability of HMnO_4 , and many others.

I would like just to point out in this connection that these errors may be of a positive as well as of a negative character, that consequently a method where, under certain circumstances, two or more simultaneously occurring inaccuracies exactly counterbalance each other may give very satisfactory results, while in other cases it may leave much, very much perhaps, to be desired, a circumstance which must be taken into consideration in the testing of analytical methods.

Thus, to select a widely-known instance, barium sulphate is not altogether insoluble in ferric chloride, and results would be obtained which would be too low if, in the determination of sulphur, after its complete oxidation to sulphuric acid, it were precipitated with barium chloride in the solution containing ferric chloride. On the other hand, the precipitate obtained in this case is not pure, as it always contains included iron salts in smaller or larger quantity, and this again leads to too

Percentage Composition of the various Glasses.

Variety of Glass.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Silica	76'22	74'09	76'39	68'56	74'48	74'69	66'75	74'12	77'07	74'40
Alumina	—	0'40	0'50	1'85	0'50	0'45	1'31	0'50	0'30	0'70
Lime	4'27	5'85	5'50	7'60	7'15	7'85	13'37	8'55	8'10	8'85
Potash	—	7'32	4'94	2'24	6'64	8'64	15'50	4'86	3'75	4'40
Soda	19'51	12'34	12'67	19'75	11'23	8'37	3'07	11'97	10'78	11'65
Totals	100'00	100'00	100'00	100'00	100'00	100'00	100'00	100'00	100'00	100'00
Silica : lime : alkali	17:1:4	11:1:2'6	12'7:1:2	10:1:3	9'5:1:2	8'8:1:1'6	4'5:1:0'8	8:1:1'6	8'8:1:1'5	8:1:1'5

Loss of Weight in Milligrammes of a 100 c.c. Flask by the action of—

Variety of Glass.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Water, 5 hours ..	62'5	31'5	29'5	17	13	9'5	7'5	7'5	5	4'5
H_2SO_4 , 25%, 3 hrs.	?	43'5	35	8	7	6'5	5'5	5	5	3
HCl , 12%, 3 hours ..	85	?	21	4	2'5	1'5	1	1	0	0
NH_3 , 10%, 3 hours ..	?	?	62	11	8'5	7'5	7'5	6	5	5
Sodium phosphate, 2%, 3 hours ..	?	?	81	64	40	35'5	34	30	15	12'5
Sodium carbonate, 2%, 3 hours ..	283	160	130	124	50'5	45	42	42	26'5	25

high results. In certain circumstances both these sources of error may more or less exactly counterbalance each other, while in others one or the other may get the upper hand, and the result consequently be either too high or too low, as the case may be. Indeed A. Tamm (*Fernkontorets Annaler*, 1887, p. 4) has based on this circumstance a rapid method for the determination of sulphur.

These occurrences—and they are not always so simple as in the above example—necessitate the most complete investigation, if with certainty either all errors are to be avoided or the most complete possible balance of errors effected, which in many cases leads to exceedingly useful methods.

6. *Personal Errors.*—The errors, too, which are due to this cause are of great importance, especially where the analyses are not effected by trained chemists, but their intimate study is beset with great difficulties. To effect this, a series of parallel analyses should be made by different chemists, using the same method, and with exact and detailed specifications as to the method of working, and as a result in all probability "personal equations" would be obtained, such as have long been known to astronomers.

These personal errors, which have their origin partly in the particular skill of the one or the other in different methods and operations, partly in personal estimations, as in the colorimetric methods, or in other causes, are, however, of particular interest, because it is just these which lead one chemist to prefer one method and another a different one, and not infrequently cause opinions as to one and the same method to be very different.

To these personal errors various occurrences may be referred, as, for instance, the following, mentioned by C. B. Dudley (*Journal of Analytical and Applied Chemistry*, 1893, p. 5):—In a sample of steel Drown found 0.14 per cent of silicon, while on the other hand another chemist found 0.28. A further investigation showed that the first-named chemist had allowed the dish to stand for two days after evaporation and taking up again with water, and had only then filtered off the silica. It was found that the silica had slowly passed into solution again. After two days of 0.28 per cent of silica only 0.14 was present, and after six days only 0.06, a behaviour which would not have been anticipated.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

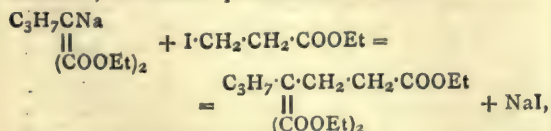
Ordinary Meeting, June 18th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 108).

97. "The Action of Ethylic β -Iodopropionate on the Sodium Derivative of Ethylic Isopropylmalonate." By J. Z. HEINKE and W. H. PERKIN, jun., F.R.S.

These experiments were instituted with the object of obtaining additional evidence as to the constitution of the isopropyl glutaric acid described in the preceding abstract. When ethylic β -iodopropionate is digested in alcoholic solution with the sodium derivative of ethylic isopropylmalonate, the reaction proceeds as follows:—

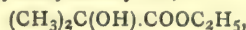


and the product formed was found to be identical with the ethylic isopropylpropanetricarboxylate described in the preceding abstract. The ethereal salt on hydrolysis

yielded isopropylpropanetricarboxylic acid (m. p. 165°), and this at 180° yielded isopropylglutaric acid (m. p. 94—95°). A number of derivatives of this acid were prepared, and in this way its identity with the isopropylglutaric acid described in the preceding abstract was conclusively proved.

98. "The Condensation of Halogen Derivatives of Fatty Ethereal Salts with Ketones and Ketonic Acids." By W. H. PERKIN, jun., F.R.S., and J. F. THORPE.

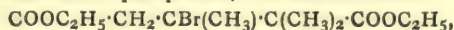
The condensation of substance containing the group >CO with halogen derivatives in the presence of zinc appears to have been first studied by Frankland and Duppa (*Annalen*, cxxxiii., 80); these chemists synthesised ethylic hydroxyisobutyrate,—



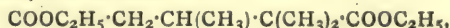
by acting on a mixture of methylic iodide and ethylic oxalate with zinc.

Since then work has been done on this condensation by several chemists, and quite lately by Reformatzky (*Ber.*, 1895, xxviii., 2838), and we have lately employed it with success in preparing the following interesting substances, of which we give a brief account, in order to reserve them for further investigation in the autumn.

(1) $\text{COOC}_2\text{H}_5\cdot\text{CH}_2\cdot\text{C}(\text{OH})(\text{CH}_3)\cdot\text{C}(\text{CH}_3)_2\cdot\text{COOC}_2\text{H}_5$, ethylic β -hydroxy- $\alpha\alpha\beta$ -trimethylglutarate, is produced by the action of zinc on a mixture of ethylacetoacetate and ethylic α -bromoisobutyrate, or of ethylic bromoacetate and ethylic dimethylacetoacetate. It is a thick colourless oil which boils at 165° (35 m.m.), and which, on hydrolysis, is decomposed, with formation of acetic and isobutyric acids. When treated with a mixture of tribromide and pentabromide of phosphorus, it is converted into—

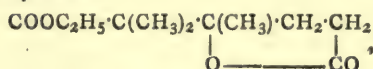


ethylic β -bromo- $\alpha\alpha\beta$ -trimethylglutarate, which distils with slight decomposition at 170—175° (30 m.m.), and, when digested with potassium cyanide in alcoholic solution, is reduced, with formation of—



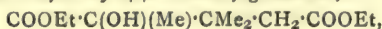
ethylic $\alpha\alpha\beta$ -trimethylglutarate. This ethereal salt boils at 162° (40 m.m.), and, on hydrolysis, yields $\alpha\alpha\beta$ -trimethylglutaric acid, a colourless crystalline substance, which melts at 147°.

(2) The ethereal salt of the lactone of $\alpha\alpha\beta$ -trimethyl- β -hydroxyadipic acid.—



is produced by distilling the product of the condensation of ethylic levulinate and ethylic bromoisobutyrate. It boils at 187—188° (30 m.m.), and dissolves in ammonia and aqueous potash, being precipitated on the addition of acids unchanged. When hydrolysed with aqueous potash at 0°, it yields the corresponding acid, a colourless crystalline substance, which melts at 105—106°.

(3) Ethylic pyruvate and ethylic β -bromoisovalerate condense readily in the presence of zinc, with formation of ethylic α -hydroxy $\alpha\beta\beta$ -trimethylglutarate,—



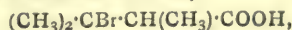
a colourless oil, which boils at 160—170° (60 m.m.).

(4) Ethyl α -methyl- β -hydroxyvalerate,—



is produced by the condensation of ethylic bromopropionate with acetone. It is a colourless oil, which distils at 105° (30 m.m.), and, on hydrolysis, yields the corresponding α -methyl- β -hydroxyvaleric acid, a thick colourless syrup, boiling at 160° (35 m.m.). From this acid the following derivatives have been prepared:—

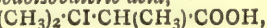
α -Methyl- β -bromisovaleric acid,—



a white crystalline solid, melting at 79°, and yielding an

oil ethereal salt, which distills in a vacuum almost without decomposition.

α-Methyl-β-iodoisovaleric acid,—



melts at 81° .

Trimethylacrylic acid, $(\text{CH}_3)_2\text{C}(\text{CH}_3)\text{COOH}$, is formed by the hydrolysis of *ethyl α-methyl-β-bromoisovalerate* with alcoholic potash. It crystallises from water in colourless prisms, which melt at $70-71^\circ$, and distills without decomposition at $145-150^\circ$ (50 m.m.). It combines with bromine, readily yielding dibromotrimethylpropionic acid, $(\text{CH}_3)_2\text{CBrCHBrCOOH}$, melting at 190° .

99. "The Electrolysis of the Salts of Monhydroxy Acids." By J. WALLACE WALKER, M.A., Ph.D.

An unsuccessful attempt was made to synthesise the alcohols of the glycolic series by electrolysis of strong solutions of the salts of the monhydroxy-acids.

100. "The Action of Formic Aldehyde on Phenylhydrazine, and on some Hydrazones." By J. WALLACE WALKER, M.A., Ph.D.

Beside the already known compound, $(\text{C}_6\text{H}_5\text{N}_2)_2(\text{CH}_2)_3$, obtained by the interaction of these substances, the author has prepared a number of others by varying the conditions of the reaction. The relationships of the different substances is fully discussed in the paper.

101. "The Colouring-matter of Sicilian Sumach, *Rhus coriaria*." By A. G. PERKIN and GEORGE YOUNG ALLEN.

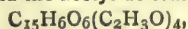
Sumach, which consists of the dried and powdered leaves of the genus *Rhus*, especially *R. coriaria* (Sicilian) and *R. cotinus* (Venetian sumach), is used in tanning, and also in dyeing and calico-printing, on account of the tannin matter it contains, which according to Löwe is gallotannic acid (Fresenius, *Zeit. Anal. Chem.*, xii., 128). According also to Chevreul it contains a yellow colouring-matter (Watts, *Dict. Chem.*, 1874, v., 614. Löwe (*Zeit. Anal. Chem.*, xii., 127), who examined the different varieties of sumach, stated that they contained quercetin and quercitrin, but this is certainly incorrect as regards Sicilian sumach.

The colouring-matter, $\text{C}_{15}\text{H}_{10}\text{O}_8$, forms glistening yellow needles, having dyeing properties similar to those of quercetin and fisetin, but is distinguished from these by its colour reactions with dilute alkalis. The sulphuric acid compound, $\text{C}_{15}\text{H}_{10}\text{O}_8\cdot\text{H}_2\text{SO}_4$, forms orange-red needles, and the acetyl derivative, $\text{C}_{15}\text{H}_4\text{O}_8(\text{C}_2\text{H}_3\text{O})_6$, colourless needles, m. p. $203-204^\circ$. Fused with alkali, it yields *phloroglucol* and *gallic acid*. These reactions show it to be identical with *myricetin*, the colouring-matter of *Myrica nagi* (see previous abstract). Sicilian sumach also contains some quantity of free gallic acid.

102. "The Colouring-matter of *Querbracho colorado*." By ARTHUR G. PERKIN and OSWALD GUNNELL.

The wood of *Querbracho colorado* constitutes the tannin matter "querbracho," which is suitable for the production of Morocco leather, and, moreover, in conjunction with alum, it gives the leather a bright yellow shade, instead of the darker colours prepared in the ordinary way. Jean (*Bull. Soc. Chim.*, xxxiii., 6) found it to contain a tannin differing from those of oak bark and chestnut wood. According to Arnaudon (Watts, *Dict. Chem.*, viii., 1732) it contains a yellow colouring-matter.

The colouring-matter, $\text{C}_{15}\text{H}_{10}\text{O}_6$, forms glistening yellow needles, dyeing shades similar to those of quercetin, and yielding compounds with mineral acids. The benzoyl derivative, $\text{C}_{15}\text{H}_6\text{O}_6(\text{C}_7\text{H}_5\text{O})_4$, colourless needles, m. p. $180-181^\circ$, and the acetyl derivative,—



colourless needles, m. p. $196-198^\circ$, were prepared. Fused with alkali it yields *protocatechuic acid*, and probably *resorcinol*. Its dyeing properties were identical with those of fisetin, $\text{C}_{15}\text{H}_{10}\text{O}_6$, the colouring-matter of young fustic (*Rhus cotinus*), and there could be little doubt that it was fisetin.

A second substance, $\text{C}_{14}\text{H}_{10}\text{O}_{10}$, forming minute prisms,

was also isolated, and was found to be *ellagic acid*, and further, the presence of a considerable quantity of *gallic acid* was detected, these latter being, no doubt, chiefly formed during the isolation of the fisetin from the querbracho.

103. "On Atisine, the Alkaloid of *Aconitum heterophyllum*." By H. A. D. JOWETT, D.Sc.

The author has investigated the nature and properties of the alkaloid contained in the roots of the non-toxic *Aconitum heterophyllum*. This alkaloid was examined by Broughton in 1873, who named it atisine, and ascribed to it the formula $\text{C}_{46}\text{H}_{74}\text{N}_2\text{O}_5$; it was subsequently examined by Wasowicz and by Alder Wright. The powdered roots were extracted by percolation with a mixture of methyl and amyl alcohol, and from this percolate was obtained the crystalline hydrochloride or hydriodide by the method described in the paper.

Atisine, for which the author adopts the formula $\text{C}_{22}\text{H}_{31}\text{NO}_2$, could only be obtained as a colourless varnish, soluble in alcohol, ether, or chloroform, slightly soluble in water, and insoluble in petroleum ether. Its alcoholic solution is laevorotatory, $[\alpha]_D = -19.6$, and though the base is amorphous it yields a series of crystalline salts.

Atisine hydrochloride, $\text{C}_{22}\text{H}_{31}\text{NO}_2\cdot\text{HCl}$, crystallises either from water or from a mixture of alcohol and ether in well-defined prisms, which melt at 296° (corr.) and are freely soluble in water or alcohol, but insoluble in ether. The aqueous solution of the salt is dextrorotatory, $[\alpha]_D = +18.46^\circ$.

Atisine hydrobromide, $\text{C}_{22}\text{H}_{31}\text{NO}_2\cdot\text{HBr}$, crystallises from water or a mixture of alcohol and ether, either singly or in rosettes of needles, which melt at 273° (corr.). The salt is freely soluble in water and alcohol, but insoluble in ether or petroleum ether, and in aqueous solution is dextrorotatory, $[\alpha]_D = +24.3^\circ$.

Atisine hydriodide, $\text{C}_{22}\text{H}_{31}\text{NO}_2\cdot\text{HI}$, crystallises from hot water or alcohol in well-defined plates or tables, melting at $279-280^\circ$ (corr.), soluble in hot water or alcohol, but sparingly soluble in cold water. Its aqueous solution is dextrorotatory, $[\alpha]_D = +27.4^\circ$. This salt cannot apparently be prepared by the direct action of hydrogen iodide upon the base, but is easily prepared by precipitating a solution of any salt of atisine with potassium mercuric iodide, and decomposing the precipitate with hydrogen sulphide.

The *nitrate* (m. p. 252° , corr.) and *platinichloride* (m. p. 229° , corr.) were also obtained as well-defined crystalline salts, but the *aureichloride* could only be obtained as an amorphous powder. The results of the analyses of a number of pure salts led to the adoption of the formula $\text{C}_{22}\text{H}_{31}\text{NO}_2$ for the base.

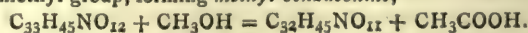
The hydriodide, when treated with hydrogen iodide, yielded no methyl iodide, and thus the alkaloid was shown to contain no methoxyl groups.

When either the base or its salts are mixed with alkalis or acids in either alcoholic or aqueous solution, no fission of the molecule takes place, but a new base, atisine monohydrate, $\text{C}_{22}\text{H}_{31}\text{NO}_2\cdot\text{H}_2\text{O}$, is formed. Neither this base nor any of its salts could be obtained in the crystalline condition, but analyses of the *aureichloride* and *platinichloride* confirmed the formula given above.

A preliminary examination of the physiological action of the nitrate by Dr. Cash, F.R.S., showed that the alkaloid is non-toxic, and that its action somewhat resembles aconitine.

104. "The Action of Methyl Alcohol on Aconitine. Formation of Methyl Benzaconine." By WYNDHAM R. DUNSTAN, F.R.S., THOMAS TICKLE, and D. H. JACKSON, Ph.D.

When aconitine (or a salt) is heated with methyl alcohol in a closed tube between $120-130^\circ$, the alkaloid loses one molecular proportion of acetic acid and takes up one methyl group, forming *methyl benzaconine*,—



The composition of the new base has been ascertained by combustion, and verified by estimation of the quantity of acetic acid separated in its production from aconitine, by estimation of the amount of benzoic acid separated on hydrolysis, and also by the determination of the number of methoxyl groups present, which has shown that the base contains one more than aconitine.

Methyl benzaconine is a well-crystallised base (m. p. 210—211°, corr.), soluble in alcohol ether and benzene, and most readily crystallised by adding light petroleum to its ethereal solution. It forms crystalline salts; the hydrochloride and the hydrobromide have been examined.

On hydrolysis, methyl benzaconine loses benzoic acid, forming a base which appears to be methyl aconine, but has not so far been completely investigated. Methyl benzaconine produces a well-marked physiological effect when administered to animals, but, unlike aconitine, it is not a powerful poison.

The authors are at present engaged in investigating the mechanism of the remarkable reaction which has led to the formation of this alkaloid, the acetyl group of aconitine being apparently replaced by methyl.

105. "The Chemical Inactivity of Röntgen Rays." By H. B. DIXON and H. BRERETON BAKER.

The authors have investigated the question whether Röntgen rays are able to influence chemical change, either by starting it or by accelerating or diminishing it after it has been started by ordinary light. In all cases examined negative results were obtained. These were carbon monoxide and oxygen (dried and moist), hydrogen and oxygen, hydrogen and chlorine, carbon monoxide and chlorine, hydrogen sulphide and sulphur dioxide, solutions of sodium sulphate and oxygen, slow oxidation of phosphorus, decomposition of hydrogen peroxide.

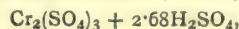
106. "Colloidal Chromsulphuric Acid." By H. T. CALVERT and T. EWAN.

By heating together one molecular proportion of chromium sulphate and four to six molecular proportions of sulphuric acid at 115° for one or two days, Recoura (*Ann. Chim. Phys.*, 1895, [7], iv., 516) has prepared a series of bodies having the formulæ $\text{Cr}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{SO}_4$, $\text{Cr}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{SO}_4$, &c., which he calls chromopolysulphuric acids. These compounds dissolve readily in water, yielding yellowish-green opalescent solutions. The behaviour of these solutions makes it appear probable that the chromosulphuric acids do not exist in them as such, but are hydrolysed, forming a colloidal substance, $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$, and free sulphuric acid. Recoura does not attempt to decide whether this is so or not. Experiments recently made by W. R. Whitney (*Zeit. Physik. Chem.*, 1896, xx., 59) lead him to the conclusion that the above view is the correct one. The following experiments, which were carried out in part more than a year ago, may be of interest as yielding further evidence in the same direction.

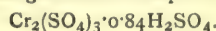
The green opalescent solutions were filtered through porous earthenware (a "Pasteur-Chamberland candle" was used). A dark green gelatinous deposit remained on the outside of the pot; the filtrate was almost colourless, and contained a mere trace of chromium together with the excess of sulphuric acid over and above that required to form the compound $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$. There was thus no doubt that the gelatinous substance removed from the solution possessed this composition; the same body was obtained from acids of the formulæ $\text{Cr}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{SO}_4$ and $\text{Cr}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{SO}_4$.

The following are the details of the experiments:—Chromium sulphate was prepared by reducing chromic acid with pure alcohol in presence of sulphuric acid (Traube, *Annalen*, 1848, lxi., 168). It was re-crystallised by precipitating its aqueous solution with alcohol, and dried in a vacuum. On prolonged heating to 200° it lost about 11 mols. of water; a determination of the sulphuric acid, however, showed that its formula was $\text{Cr}_2(\text{SO}_4)_3 \cdot 12 \cdot 75\text{H}_2\text{O}$.

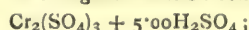
I. One molecule of this salt was mixed with 3 mols. of concentrated sulphuric acid, and the mixture heated to 115—120° for seven days. The mass dissolved readily in water; 10 c.c. of the pale green opalescent solution yielded 0.0596 grm. Cr_2O_3 and 0.5177 grm. BaSO_4 . The liquid was then filtered through the moist porous pot by evacuating the latter internally; the first portion of the filtrate was rejected. Since the filtration was very slow the filtrate probably became somewhat too concentrated by evaporation. 10 c.c. of the filtrate gave 0.1674 grm. BaSO_4 . The solution therefore contained—



and the filtrate contained $\text{Cr}_2(\text{SO}_4)_3 + 1.84\text{H}_2\text{SO}_4$. The composition of the gelatinous compound was—



II. This experiment was made in the same way, the results being:—The original solution contained—



the filtrate contained $\text{Cr}_2(\text{SO}_4)_3 + 4.25\text{H}_2\text{SO}_4$. The substance removed was thus $\text{Cr}_2(\text{SO}_4)_3 + 0.75\text{H}_2\text{SO}_4$.

The formation of the colloidal substance was not observed when one molecular proportion of chromium sulphate was heated with one molecular proportion of sulphuric acid for two weeks.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 6, August 10, 1896.

The Lavoisier Memorial.—A list is inserted of the subscriptions given by learned bodies and private individuals for the proposed monument. The Chemical Society of London has contributed 625 frs.; the Royal Society of Dublin, 500; and Trinity College, Dublin, 676 frs. The total hitherto received is 47553.30 frs. A further subscription is in progress, which is headed by the Emperor of Russia with 2000 roubles. The execution of the statue will be entrusted to M. Barras.

Researches on Cyanic Acid.—M. Berthelot.—A collection of thermo-chemical data. It appears that the transformation of ammonium cyanate into urea is attended with a disengagement of +8.3 cal.

Researches on the Volatility of Levulic Acid.—MM. Berthelot and André.—The point of ebullition of levulic acid is 239°. Levulic acid tends to be split up into two portions, differing in composition. The most volatile portion, forming about the half of the total product, corresponds to the formula $\text{C}_5\text{H}_8\text{O}_{3\frac{1}{2}}\text{H}_2\text{O}$. The residue is $\text{C}_5\text{H}_{10}\text{O}_4$ (dioxylvaleic acid).

Reactions exerted in the Cold between Phosphoric Acid and Ether in presence of Water. Coefficient of Distribution.—M. Berthelot and G. André.—Setting out with an acid of 0.434 grm. per c.c., an aqueous solution of phosphoric acid gives up merely an insignificant quantity of acid to the ether with which it is agitated.

Part Played by the Dielectric in the Discharge of Röntgen's Rays.—Jean Perrin.—This paper requires the two accompanying figures.

No. 7, August 17, 1896.

On the Copper Mines of Sinai, worked by the Ancient Egyptians.—M. Berthelot.—The copper mines of Sinai are the most ancient of which history makes mention. According to authentic documents, they were worked since the time of the Egyptian dynasty (about

5000 years B.C.) until the end of the Ramesseïdes (about 1300 to 1200 B.C.). Their possession had been the object of several wars, but they had been abandoned for 3000 years, on account of the poverty of the ores. It was from these mines that was obtained the sceptre of Pepi I., a king of the VI. th dynasty. This sceptre, made of pure copper, of which I have made an analysis, is preserved in the British Museum. The adits still exist, as well as the ruins of the furnaces, the crucibles, the huts of the miners, and some fragments of their tools. In the specimens obtained by M. de Morgan there occur three ores: turquoise, copper hydrosilicate, and sandstones impregnated with copper. These actual ores are superficial, and form a cap, derived from the alteration of deeper pyritic beds which the ancient miners failed to reach. The turquoises contained 3.32 per cent cupric oxide; the cupriferous gritstones are equally poor. Among the débris have been found fragments of furnaces and crucibles, slags, and cinders, fragments of tools. Nor is there evidence of the use of fluxes. Some of the fragments of tools contain arsenic, which was used by the Greek and Egyptian alchemists for hardening copper. It is interesting to note that metallurgical procedures similar to those of our days had been reached empirically 7000 years ago.

Combination of Argon with Water.—P. Villard.—Argon combines with water to form a crystalline and dissociable hydrate analogous to the hydrates of gases already known, and taking rise under similar conditions. The argon being compressed to about 150 atmospheres in presence of water kept near upon 0°, it is sufficient to refrigerate a point of the tube so as to congeal at this point the water which moistens the sides of the tube, when there is produced a crystallisation which sets out from the refrigerated point. At 0° the tension of dissociation of argon hydrate is about 105 atmospheres. At +8° it reaches 210 atmospheres.

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Professor—SYDNEY YOUNG, D.Sc., F.R.S.

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Junior Demonstrator—E. HALFORD STRANGE, B.Sc.

The SESSION 1896-97 begins on October 6th. Lectures on Inorganic, Organic, and Advanced Chemistry will be delivered during the Session. The Laboratories are fitted with the most recent improvements for the study of Practical Chemistry in all its branches. In the Evening the Laboratory is opened and Lectures on Inorganic Chemistry, at reduced fees, are delivered. Several Scholarships are tenable at the College. CALENDAR, containing full information, price 1/- (by post 1/3). For Prospectus and further particulars apply to JAMES RAFTER, Secretary.

UNIVERSITY COLLEGE, NOTTINGHAM.

SESSION 1896-97.

The SESSION begins SEPTEMBER 28th.

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The Council does not bind itself to accept the lowest or any tender, and it will not accept the tender of any person or firm who shall on any previous occasion have withdrawn a tender after the same has been opened unless the reasons for the withdrawal were satisfactory to the Council.

Spring Gardens, S.W.,
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C. J. STEWART,
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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1920.

(STUDENTS' NUMBER).

ADDRESS TO STUDENTS.

THE present position and prospects of chemical science justify a few words of advice to students.

Discoveries have been lately made of a novel character, such as may possibly modify the course of future research. Thus it is very probable that argon and helium are not merely isolated bodies hitherto unknown, but that they are the types of a new class of elements which may seriously modify our general views. Hence they must require careful examination from every conceivable point of view. Technically, indeed, these elements may be of little direct moment, but their indirect bearings may be for the present beyond our ken.

The grand question of the elements as modifications of protyle, or as mere desultory and ultimate essences, has not been advanced any nearer to a definite solution, but our suspicions of their modifiable character are certainly becoming more justified. Young chemists who have time at their disposal might very advantageously employ it in this direction. The failure of Dr. S. Brown to effect a mutual conversion of carbon and silicon should not, we think, discourage us from future attempts in this direction.

A recent discovery has made us acquainted not indeed with a new form of matter, but—what is certainly of not less importance—a new modification of energy. The X rays of Prof. Röntgen have indeed proved of practical value, more than sufficient to compensate for the foolish jests which they have supplied to the literary and general papers. But higher than their value, as placing at our disposal a new analytical procedure, must rank the prospect which they hold out to us of reaching other kinds of vibrations not yet realised.

It seems that the advance which we have already accomplished in chemical and physical science, instead of narrowing, actually expands the fields which remain for us to occupy. If Science means the interpretation of the universe, its scope must widen with our comprehension of the almost infinite nature of its task. The recent collapse of China, which obstinately closed its eyes to the extension of knowledge and insisted on grovelling amidst the relics of the past, ought to be for us a final lesson.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of £2 to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of £1, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages:—Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Science:—Chemistry, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds, their chief physical and chemical characters, their preparation, and their characteristic tests.

A Pass Certificate, signed by the Registrar, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will commence on the third Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held on the third Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

The examination for Honours in Chemistry will take place on Monday, Tuesday, and Wednesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday and Wednesday by practical examination in Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with this statement he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third

Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examination, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, V. H. Veley, F.R.S., J. E. Marsh.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Christ Church Laboratory.—A. Vernon Harcourt, F.R.S.

Balliol Laboratory.—Sir J. Conroy, F.R.S., D. H. Nagel.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the examinations being in November, at Easter, and in June and October.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.
TRINITY COLLEGE.

Professor of Chemistry—J. Emerson Reynolds, D.Sc., M.D., F.R.S.

Assistant Lecturer—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—J. Percy Bailey, B.A.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 1st of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; advanced, second year.
2. *Organic Chemistry*.—General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The *Summer Course of Practical Chemistry for Medical Students* begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

KING'S COLLEGE.

(DIVISION OF ENGINEERING AND APPLIED SCIENCE).

Professor of Chemistry—J. M. Thomson, F.R.S.E., F.C.S.

Demonstrator of Practical Chemistry—Herbert Jackson, F.C.S.

Assistant Demonstrators—P. H. Kirkaldy, F.C.S., and W. H. Sodeau.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1896-97 are Tuesday, September 29, Wednesday, January 20, and Wednesday, April 28.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis. Any Student of this Division may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till

four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. od.; per ann., £8 8s. od.; Practical Chemistry per term, £4 4s. od.; per ann., £10 10s. od.; Experimental and Analytical Chemistry—Daily attendance: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

METALLURGY.

Professor—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, F.R.S.E., F.C.S.

Arrangements are made for a complete Course of Instruction in Photography to the students of the third year. A glass house has been erected, and in connection with it a Laboratory for the preparation of Photographic Chemicals. Students will be afforded every facility for practising the Art in all its branches.

In addition to the regular College Course in Photography occasional classes are formed, consisting each of about six gentlemen, who meet twice a week. The fee for private instruction is £5 5s. for ten lessons, or £10 10s. for three courses. There is in every case a charge of £1 each course for chemicals.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June.

UNIVERSITY OF SCIENCE.

FACULTY OF SCIENCE.

Professor—William Ramsay, Ph.D., F.R.S.

Assistants—Morris Travers, B.Sc., Alexander Kellas, B.Sc., and J. W. Walker, B.Sc., Ph.D.

The Session is divided into three Terms, as follows, all the dates being inclusive:—

First Term, from Wednesday, October 6th, until Friday, December 18th;

Second Term, from Tuesday, January 12th, 1897, till Friday, April 2nd;

Third Term, from Tuesday, April 27th, till Friday, July 2nd. Class Examinations begin on June 21st.

Junior Courses.

First Term: Tuesday, Thursday, and Saturday at 10. Second and Third Terms: Tuesday, Thursday, and Saturday at 10, Friday at 4. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fees:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning on January 14. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday, Thursday, and Saturday, at 9, in the First Term; Tuesday, Thursday, and Saturday, at 10, in the Second Term; and Tuesday and Thursday at 9, and Saturday at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who are studying the subject from a scientific standpoint. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course besides the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for the Second and Third Terms, £4 14s. 6d.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

Junior Practical Class.

First and Second Terms, Tuesday and Thursday, at 11. Fee, including cost of materials, £5 5s.; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific and Intermediate Science Examinations.

Senior Practical Class.

Wednesdays from 2 to 4 and Saturdays from 10 to 12 during the Third Term; also Tuesdays and Thursdays from 11 to 12.

Fee:—(Including cost of materials) £5 5s.; for a Second Course, £3 3s.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent

Students on the work done during the Session. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1896-97; also the Cloth-worker's Scholarship of £30.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—W. P. Wynne, D.Sc., F.R.S.

Demonstrators—H. Chapman Jones and J. W. Rodger, A.R.C.S.

Assistants—G. S. Newth, A. Eiloart, Ph.D., B.Sc., and M. O. Forster, Ph.D.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 7th of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and in the third year those of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
	£	£
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy	4	8
Mechanics	4	6
Metallurgy	4	13
Mining	2	
Astronomical Physics	2	3

Agricultural Chemistry, per term, £13. Mathematics and Mechanical Drawing, £3 per term. Model and Free-hand Drawing, £1 per term. Descriptive Geometry, £3 per session. Mine Surveying, £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half fees.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Bona fide teachers qualified to earn payments for teaching Science according to the rule of the Science and Art Directory may obtain permission to attend free any course of lectures.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a bonus towards their incidental expenses of £3 each. (See Science and Art Directory.)

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fifty-fifth Session will commence on Monday, October 5th, 1896.

Professors—Chemistry, J. Norman Collie, Ph.D., F.R.S.; Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S.; Materia Medica and Pharmacy, Henry G. Greenish, F.I.C., F.L.S. (Dean).

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Richard Bremridge, Secretary and Registrar, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Professor—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Göttingen), F.I.C.

Assistant Lecturer and Demonstrator—A. W. Warrington, M.Sc. (Vic.), F.I.C.

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

The College is open to male and female students above the age of sixteen years. The Session commences on Tuesday, September 29, on which day all Students will

be expected to meet the Professors in the Library of the College.

Lecture Courses.—(1) Matriculation Course; three lectures weekly during the Michaelmas and two weekly during the Lent and Easter Terms. (2) Intermediate Science Pass Course; four lectures weekly during the Lent and Easter Terms. (3 and 4) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, two lectures weekly on Chemical Theory. (Courses A and B will generally be given in alternate Sessions; for 1896-7, Course A.) (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Wednesdays and Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 10s. per term, and for twelve hours, 20s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 15, and exhibitions are awarded at the end of the Session on the results of the class examinations.

The Chemical Laboratories in connection with this College have been recently built, and are fitted with every convenience for the prosecution of chemical studies.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Fred. Marsden, Ph.D., B.Sc. Assistant Lecturer in Agricultural Chemistry, F. V. Dutton.

Physics.—Professor, Andrew Gray, M.A., LL.D., F.R.S.

The Session opens September 29th, 1896. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Term £2 2s. A class for revision of

Matriculation Work will be held during the Summer Term. Fee for the Term, £1 1s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Term £2 2s.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Medical Course.—Inorganic and Organic Chemistry. Fee for the whole Course, £4 4s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor.—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrators.—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 15th, and terminates on June 23rd, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course, and is the qualifying course for the Intermediate Examination of the University of Wales. Together with laboratory practice, it will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of some 60 lectures devoted to Physical and Theoretical Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales

and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry.—Sydney Young, D.Sc., F.R.S.

Lecturer.—Francis E. Francis, B.Sc., Ph.D.

Junior Demonstrator.—E. Halford Strange, B.Sc.

The session 1896-97 will begin on October 6th. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Junior Course.—Two Lectures a week will be given during the First and Second Terms. Fee, £3 3s.

Senior Course.—Three Lectures a week will be given throughout the Session. Fee, £5 5s. There will be tutorial classes in connection with the Junior and Senior Courses.

Advanced Course.—One Lecture a week will be given throughout the Session. Fee, £2 12s. 6d.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given during the Second Term, and three Lectures a week during the Third Term. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session. Fee, £2 12s. 6d.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session ..	15	12½	10	7½	5
„ Two Terms ..	11	9	7½	5½	3½
„ One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

Practical Chemistry—Laboratory Instruction.—The Laboratory will be open on Tuesday and Thursday evenings from 7 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—(Two Terms) Two Evenings, 25s.; One Evening, 15s. (One Term) Two Evenings, 15s.; One Evening, 10s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, is. 4d.), containing detailed information of the various Courses, may be obtained on application to the Secretary.

MASON COLLEGE, BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., B.Sc., F.R.S.

Assistant Lecturer—C. F. Baker, Ph.D., B.Sc.

Demonstrator—(Vacant).

The Session will be opened on October 5th, 1896.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. Lecture days—Wednesdays and Fridays at 11.30.

Persons entirely unacquainted with Chemistry are recommended to attend this Course before entering for the General Course. Candidates for the Matriculation Examination of the University of London also are advised to attend this Course.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December, and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. A Tutorial Class is held in connection with this Course once a week throughout the Session. Fee, £5 5s. for the course.

2. May to July (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the

chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Wednesday, and Friday at 12 noon. Fee, £1 11s. 6d.

The General Course (including Inorganic and Organic lectures) qualifies for graduation in the medical faculties of the universities of Edinburgh, Glasgow, Aberdeen, and Durham.

Special Courses of Lectures and of Laboratory Instruction are given for Medical Students preparing for the Conjoint Board Examinations.

Advanced Course.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet twice a week. Fee for the session £3 3s.

Laboratory Practice.

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees:—

	All day.	Three hours per day.
One Term	7 guineas	4½ guineas.
Two Terms	13 „	8½ „
Three Terms	18 „	12 „

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each of the first two courses, and for each of the two sections of the third course. A more advanced course of about sixty lectures upon selected subjects is also given by Mr. McMillan, the Lecturer in Metallurgy.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c

Evening Classes.

Special Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of £100 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of £100 is awarded annually in September.

Forster Research Scholarship.—A Scholarship of the value of £50 is annually awarded.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturer.

BRADFORD TECHNICAL COLLEGE.

CHEMISTRY AND DYEING DEPARTMENT.

Professor—W. M. Gardner, F.C.S.*Demonstrator*—A. B. Knaggs, F.C.S.*Lecturer on Botany and Biology*—William West, F.L.S.

The school year is divided into three terms. The Session commences on September 14th and terminates on July 17th. The course of instruction extends over two years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Fee, £4 per Term, or £11 per Session.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day and for pharmaceutical students.

ROYAL AGRICULTURAL COLLEGE,
CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.*Assistants*—Cecil C. Duncan, F.I.C., and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY.

THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc. Lond., F.I.C.*Lecturer in Organic Chemistry*—Julius B. Cohen, Ph.D., F.I.C.*Assistant Lecturer in Agricultural Chemistry*—Herbert Ingle, F.I.C.*Demonstrator*—Frankland Dent, B.Sc.

The Session begins October 6, 1896.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m., from October to the end of the second term, and during part of the third term. Fee for the Course, £4 4s.

2. Inorganic Chemistry.—First year Honours Course, Non-metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Inorganic Chemistry.—Second year Honours Course, Metals. Tuesday, Thursday, and Saturday at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 12 noon. Fee £3 13s. 6d.

5. Organic Chemistry Honours Course.—Wednesday and Friday at 12 noon. Fee, £2 12s. 6d.

6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.

7. Chemistry as Applied to Coal Mining.—Tuesday during the First Term, at 4 p.m.

8. Agricultural Chemistry.—Monday, Tuesday, and Friday, at 3 p.m., during first and second terms.

9. Chemistry for Teachers.—Saturdays from 9.30 to 12.30 in the first and second terms. Fee, £4 4s.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Chemistry for Medical Students.—Tuesdays, 9.30 to 11.30 October to end of December; Thursdays, 2 to 4 from January to end of March.

Practical Course in Sanitary Chemistry.—At times to be arranged.

Practical Organic Chemistry for Medical Students.—At times to be arranged.

Evening Class.

A Course of twenty Lectures by Mr. Ingle, on the Chemistry of Engineering will begin during the first and second Terms. Fee, 10s. 6d.

Dyeing Department.

Professor—J. J. Hummel, F.I.C.*Lecturer and Research Assistant*—A. G. Perkin, F.R.S.E.*Assistant Lecturer*—W. M. Gardner.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, F.I.C.

The full Course, which extends over a period of three years, is suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and is recommended to sons of tanners. The Course includes instruction in chemistry, engineering, leather manufacture, and practical work in the Leather Industries Laboratory.

Agricultural Department.

Professor—James Muir.

The full Course occupies two years, and includes instruction in chemistry, physics, botany, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, Emsley, Craven, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition, and one of the 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor—J. Campbell Brown, D.Sc.*Lecturer on Organic Chemistry*—C. A. Kohn, B.Sc., Ph.D.*Lecturer on Metallurgy*—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers—T. L. Bailey, Ph.D., C. A. Kohn, B.Sc., Ph.D., S. B. Schryver, B.Sc., Ph.D., and A. W. Titherley, B.Sc., Ph.D.

Assistant—H. H. Froyseil.

The Session commences October 5th.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or

for the M.Sc. or D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for the Pharmaceutical Diplomas; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, £4.

Dental Course, Lectures and Practical. Fee, £5 5s.

Course A.—Non-metals. Fee, £3 10s.

Course B.—Metals. Fee, £3 10s.

Course C.—Organic Chemistry. Fee, £3 10s.

Course H.—Special Organic Subjects. Fee, £1.

Course D.—Physical Chemistry. One Term. Fee, £1.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F.—Technological Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) Copper, Iron, and Steel. (3) Lead, Silver and Gold, Aluminium, and other Metals. (4) Distillation of Coal and Tar Industries. (5) Fuel and Gas. (6) Chemistry Applied to Sanitation. (7) Technical Gas Analysis. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Revision Class. (4) Senior: Practical Organic (Advanced Medical Class). (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Saitanry subjects, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class: Course arranged to suit the requirements of the London University B.Sc. Examinations, Pass and Honours, and for Intermediate M.B. Honours.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical work.

An additional metallurgy room with furnaces has been built, and an Electrochemical department has been added.

The William Gossage Laboratory will be opened during the winter of 1896. This consists of a large and well-fitted general Laboratory for advanced Students, a new gas analysis room, an additional lecture-room for Metallurgy and other classes, and an addition to the Research Laboratory. New stores for students' apparatus and chemicals will be opened in October.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day	£4	£8
Two days	6	10
Three days	8	12
Four days	9	15
Whole week	10 10s.	21

Pharmaceutical Course, £11.

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, or Physics. Elementary Engineering, Drawing, and Design (in this or one of the following years). German.

Or the Victoria Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Practical Organic Class during the Summer Term; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Course C, on Organic Chemistry, Lecture Course E or D, Technological Chemistry, Course F, on Metallurgy. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—Courses D, F, and C. Any other Courses omitted in a previous year. Laboratory, five days per week. Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Association of the Institute of Chemistry of Great Britain and Ireland may be taken. Three years study after passing the Preliminary Examination of Victoria University are required for the B.Sc. Degree in the Honours School of Chemistry.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1895, on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held on Metallurgy and on Analysis of Gases.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

DURHAM COLLEGE OF SCIENCE,
NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—Saville Shaw, F.C.S.

Lecturer in Agricultural Chemistry—R. Greig Smith, B.Sc. (Edin.), F.C.S.

Assistant Lecturer and Demonstrator—F. C. Garrett, M.Sc., F.C.S.

The Session will commence on September 28th, 1896.

1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 7th. Fee, £3 10s. for the Session.

2. *Advanced Course.*—Inorganic Chemistry, Tuesdays 3 to 4 p.m., during the Session. Fee, £2; or for students taking Organic Chemistry, £1.

3. *Organic Chemistry.*—A Course of Lectures will be given throughout the Session, the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a.m., and Fridays 3 to 4 p.m., and will commence on Thursday, October 8th. Fee, £3 10s. for the Session.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m.

Metallurgy and Assaying.—Lecturer, Saville Shaw, F.C.S. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry-Assaying, and in the preparation and analysis of Alloys, &c. Fee as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. **Laboratory Fees.**—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.
2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Physical Science.—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year. Associates in Science are admissible one year after obtaining the title of Associate to examination for the degree of Bachelor of Science of the University of Durham.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 28th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students.

OWENS COLLEGE, VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers—George H. Bailey, D.Sc., Ph.D.; Arthur Harden, M.Sc., Ph.D.; P. J. Hartog, B.Sc.; B. Lean, B.A., D.Sc.; and E. Haworth, B.Sc.

Lecturer in Technical Organic Chemistry—Dr. J. Thorpe.
Assistant Lecturer in Metallurgy—(Vacant).

The Session begins on October 6, 1896, and ends on July 3, 1897.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, Fridays, 3.30 p.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (General).—Tuesdays and Thursdays, 9.30, during two Winter Terms.

Organic Chemistry (Honours).—Mondays and Fridays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 10.30, during the Session.

METALLURGY.—**Lectures:** The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. **Practical:** Saturdays, 9.30.

The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—

First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £150 is awarded annually among the Graduates in Science for the encouragement of Research. Among the College Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; the John Buckley Scholarship; &c.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—Natural and Artificial Dye-stuffs, and the Principles of Dyeing and Printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—Frank Clowes, D.Sc., Lond., F.I.C.

Demonstrators of Chemistry—J. J. Sudborough, D.Sc., Ph.D., F.I.C.; R. M. Caven, B.Sc., F.I.C.; and G. Meland, B.Sc., A.R.S.M., F.I.C.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on Monday, September 28th.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Non-Metals for the first two terms and for Elementary Organic Chemistry in the third term. In his second year he takes the course on Metals for the first two terms. In his third year he attends a course on Advanced Organic Chemistry or Applied Chemistry. Fee for Day Lectures and Classes: Non-Metals or Metals 42s.; Organic Chemistry (one term) 21s.; Advanced Organic Chemistry, 21s. per term.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 5s.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry.—The chemical laboratory is open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1, and on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For

evening students, 10s. for two hours per week, three hours 15s., four hours 20s., six hours 30s., per term.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students can at all times work in the Chemical Laboratory, taking work suitable for the preparation for the Minor Examinations. Special lectures will also be given in Chemistry and Materia Medica.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonstrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in September. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

An Agricultural Course of instruction, extending over two years, is now organised under the general direction of Mr. M. J. R. Dunstan, M.A., F.R.S.E. It includes instruction in chemistry, botany, agriculture, with practical work on experimental fields, dairy work, farriery, land surveying, &c. The instruction is designed for those who intend to become farmers, bailiffs, land agents, or colonists, and may be extended to a third year if desired. Fee, £15 per annum for residents in Notts, £20 to residents in other counties.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

FIRTH COLLEGE, SHEFFIELD.

Professor of Chemistry—W. Carleton Williams, B.Sc., F.C.S.

Demonstrators and Assistant Lecturers—G. Young, Ph.D., and L. T. O'Shea, B.Sc., F.C.S.,

The Session will commence on October 7th.

First Course.—Chemistry of the Non-Metallic Elements. Tuesday and Friday from 10 to 11 a.m. Fee, £2 12s. 6d.

Second Course.—Chemistry of Metals. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Third Course.—Inorganic Chemistry, Honours Course, Monday, 3. Fee, £1 11s. 6d.

Fourth Course.—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 12s. 6d. Chemical Philosophy, Thursday, 11 to 12. Fee, £1 11s. 6d.

Fifth Course.—Organic Chemistry, Honours Course, Thursday, 4. Fee, £1 11s. 6d.

Short Courses of Lectures are also given by L. T. O'Shea on Electrolytic Analysis, the Chemistry of Coal Mining, and on Thermic Chemistry.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Students who have worked for three sessions in the

Chemical Laboratory are eligible for election to a scholarship value £150 for two years.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s.

UNIVERSITY COLLEGE, DUNDEE.

Professor of Chemistry—James Walker, Ph.D., D.Sc.

Assistant Lecturers—F. J. Hambly, F.I.C., and J. R. Appleyard, F.C.S.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins on October 12th, and ends in March. The Summer Session extends from the middle of April to the end of June.

The First Year's Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. To supplement the Practical work of First Year's Laboratory Students a short course of Lectures on *Analytical Chemistry* will be offered. Special facilities are afforded to Research Students.

The Lectures and Laboratory Practice in Chemistry are recognised by the Medical Colleges of London and Edinburgh, as well as by the Universities of Edinburgh and Glasgow, for degrees in Science and Medicine. The Courses are suitable for the degrees of the University of London and for the Civil Service appointments, and will also satisfy the requirements of Students in Pharmacy, and of Students who intend to become candidates for the Associateship of the Institute of Chemistry, as far as qualification in Chemistry is concerned.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S., Pres. C.S.

Lecturers—L. Dobbin, Ph.D., and H. Marshall, D.Sc.

Assistant—W. W. Taylor, M.A.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to end of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. A class on Organic Chemistry is held in summer; fee, £2 2s. There is also a class on Chemical Theory, by Dr. Dobbin; fee £1 1s.: and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are given by the Assistants on some particular branch of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s., Oct.-Dec., Jan.-March; or Summer Session, £5 5s. Half Day—Winter Session, £6 6s., Oct.-

Dec., Jan.-March; or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Second B.Sc. Examination includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy, including Anthropology, Physiology, Geology, including Mineralogy, Zoology, including Comparative Anatomy, and Botany, including Vegetable Physiology. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Physical Chemistry; Chemical Crystallography; History of Chemistry. Practical Examination:—Complex Qualitative Analysis; Quantitative Analysis, including Gas Analysis and Organic Analysis; Preparation of Pure Substances, organic and inorganic; Physico-chemical Measurements.

In the Courses for Final Examination in Pure Science, two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Professor—John Gibson, Ph.D., F.R.S.E.

Assistant Professor—John E. Mackenzie, Ph.D., B.Sc.

Demonstrators—Andrew F. King and James B. Shand. The Session begins October 6th, 1896.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Lecture Course to day students in Chemistry is mainly devoted to Inorganic Chemistry. In the Laboratory course each student is required to prepare and study the properties of the principal elementary and compound gases; to perform the more important experiments shown by the Professor in the Lecture Room; to make himself thoroughly acquainted with the preparation and purification

tion of a number of salts. After a careful study of the reactions of the principal metals and acids, he passes on to a full course of systematic qualitative analysis, and may then, if attending a second year, take up an extensive course of quantitative analysis (gravimetric, volumetric, and electrolytic), ultimately making a speciality of any branch of the subject which may be most necessary for his future work. Great attention has been paid to the thorough equipment of the Advanced Laboratories, and special facilities are given to advanced students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely chemical or of a technical nature.

The teaching in the Evening Classes is based on the Syllabus of the Science and Art Department, and includes Elementary, Advanced, and Honours Courses in Theoretical and Practical Inorganic and Organic Chemistry.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.
Professor of Technical Chemistry—E. J. Mills, D.Sc., F.R.S.

Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction in Metallurgy and Mining will be given in both Day and Evening Classes.

Copies of the Calendar for 1896-97 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

UNIVERSITY OF ST. ANDREWS.
UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.
Professor of Chemistry—T. Purdie, B.Sc., Ph.D., F.R.S.

The Session begins on October 7th. A Competitive Examination, open to intending Students of Arts or Science, for about fifty Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 26th and following days. About twenty of these Bursaries are restricted to Men and thirty to Women, twenty of the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. Two are open to students of either sex. Two Scholarships of £100 each, tenable for one year, will be open for competition to Graduates of Science at the close of Session 1895-96. A Hall of Residence is provided for Women Students. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment. The Lectures are supplemented by a short Course of Laboratory Practice, intended to illustrate the principles of the science.

These courses of instruction are intended to meet the requirements of the Arts' Curriculum; also of candidates for the First B.Sc. Examination, and of students of medicine, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part treats of the General Principles and Theory of Chemistry, and of more advanced Inorganic Chemistry, the instruction in general being such as is required for the Second B.Sc. Examination.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—

(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the First and Second B.Sc. Examinations, and for Students of Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly. A certain number of working places in the Laboratory will be available without fee for students who are capable of undertaking original investigation.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.S.E., &c.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week until the beginning of April, and on three days of each week after May 1st, at 2 p.m. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

Scholarships.—In addition to various Scholarships awarded in the Faculties of Arts and Medicine in which Chemistry forms a part of the examination, there are other valuable Scholarships awarded specially in connection with the schools of Chemistry and Physics,

QUEEN'S COLLEGE, CORK.

Professor—Augustus E. Dixon, M.D.*Demonstrator*—R. E. Doran, F.C.S.

The College Session begins on October 20th, 1896, and ends on June 12th, 1897. The classes are open to male and female students.

Systematic Chemistry.—(1) General course of Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.—Fee for each Sessional Course, £2. Each subsequent Course, £1. (2) Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.—(1) The General Course of Practical Chemistry, consisting of about forty Lectures, begins on January 4th, 1897. Fee for each Sessional Course, £3. (2) It is contemplated to also hold a Summer Course of Practical Chemistry, commencing in March. Students desiring to attend this Course must send their names to the Registrar on or before the 30th November, 1896, in order to allow the final arrangements to be published before Christmas. (3) A Course for Pharmaceutical Students. (4) Special Courses.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senior, Ph.D., M.D., F.I.C.*Demonstrator*—A. J. Walker, B.A.

The College Session is divided into three terms. The First Term extends from October 20 to December 23, the Second Term from January 7 to April 10, and the Third Term from April 26 to June 12.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—1. First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—1. First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.*—1. Second year's Course, Inorganic and Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

For Fees and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE FOR IRELAND,
STEPHEN'S GREEN, DUBLIN.

(SCIENCE AND ART DEPARTMENT).

Professor of Chemistry—W. N. Hartley, F.R.S.*Assistant Chemist*—Hugh Ramage, F.I.C., Associate of the Royal College of Science, Dublin.*Demonstrator of Chemistry and Assaying*—J. Holms Pollok, B.Sc.

The Session commences on Tuesday, October 6th, 1896.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures, Physics, and Natural Science. The Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Chemical Manufactures and Metallurgy; (3) Analytical and Experimental Chemistry; (4) Instructions in Chemical Research.

Fees payable by Non-Associates:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month; £5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months £12 for the entire session.

NOTE.—Important changes have been made in the Curriculum for Associate Students. Full particulars are contained in the Directory of the College, which may be had on application to the Secretary.

The following are supplementary courses of instruction arranged for those who are attending a Course of Lectures:—

- (1) Laboratory Instruction in the Theory of Chemistry.
- (2) An Analytical Course for Students in Engineering.
- (3) A Course of Practical Chemistry for Medical Students.
- (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health.
- (5) Assaying.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Examinations of the Department of Science and Art.

CHEMICAL LECTURES, CLASSES, AND
LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 10d., net.—*City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of industry, whether Manu-

factures or Arts. The main purpose of the instruction given is to point out the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations will begin on Monday, Sept. 21st, and the Winter Session opens on Tuesday, October 7th. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College at 10 o'clock on Tuesday, September 22nd, 1896. *South London Technical Art School.*—Classes in Modelling, Design, Wood Engraving, Drawing and Painting, House Decoration, Machine Drawing and Design, Plaster-work, &c.

CITY OF LONDON COLLEGE, White Street, Moorfields.—Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, conducted by Mr. I. S. Scarf, F.I.C., F.C.S., assisted by Messrs. J. Davis, H. V. Butfield, F.C.S., and C. A. West. Session commences Oct. 1.

BATTERSEA POLYTECHNIC.—Principal, Mr. Sidney H. Wells, Wh. Sc. Inorganic, Organic, and Technological Chemistry, Mr. W. A. Bone, M.Sc. (Vict.), Ph.D., assisted by Mr. J. Wilson, B.Sc. (Vict.). Day and Evening Classes in Science and Art subjects.

BIRKBECK LITERARY AND SCIENTIFIC INSTITUTION, BREAM'S BUILDINGS, CHANCERY LANE.—Chemistry Courses will be conducted, commencing October 1st, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University. *Inorganic Chemistry:* Mr. J. Woodward, B.A., B.Sc. Lectures—Elementary, Tuesdays, 8.15 p.m.; Advanced, Thursdays, 6.15; Practical, Tuesdays, 6—9 p.m.; Thursdays, 7.30—9.30 p.m. *Organic Chemistry:* Mr. F. Gossling, B.Sc. Lectures—Elementary, Wednesdays, 6 to 7 p.m.; Practical, Wednesdays, 7 to 9 p.m.

THE CENTRAL SCHOOL OF CHEMISTRY AND PHARMACY, 173, Marylebone Road, London.—Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c., and Mr. Lionel Cooper, F.C.S. Lectures are given on Chemistry, Physics, Botany, Materia Medica, Pharmacy, &c. Laboratory Instruction.

SOUTH LONDON SCHOOL OF PHARMACY, Lim., 325, Kennington Road, S.E.—Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., Daily, at 12 noon. Lectures on Botany daily at 1 p.m. and at 2.30 p.m. on Materia Medica and Pharmacy, by Mr. Dodd, F.C.S. The Laboratories for Qualitative and Quantitative Analysis open daily from 9 till 5, under the direction of Mr. de Koningh, F.I.C., F.C.S. The Students' Laboratory of this Institution is specially designed to accommodate 40

Students. The Technical Laboratory is open daily from 9 till 5, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees for the first three months 12 guineas; afterwards 3 guineas per month respectively, inclusive of all departments.

SOUTH-WEST LONDON POLYTECHNIC, Mauresa Road, Chelsea.—Principal, Herbert Tomlinson, B.A., F.R.S. Technical Day Classes in Chemical Industries, commencing September 29th.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Head of the Chemistry Department, Mr. A. G. Bloxam, F.I.C.; Assistants, Mr. H. C. L. Bloxam, and others. Lectures and Practical Classes in General Chemistry, also in Chemistry applied to Gas Manufacture and other industries, are held in the evenings from 7.30 to 10.0, and are open to both sexes. Special attention is paid to Technical Laboratory work and the investigation of manufacturing difficulties.

PEOPLE'S PALACE, Mile End Road, E. (Draper's Company's Institute).—Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Assistant, Mr. F. G. Pope. The classes are open to both sexes without limit of age. Evening classes in Theoretical and Practical Chemistry. The Session commences on Monday, September 21st. A Course for the London University B.Sc. Degree, including Honours, is now offered, and the Chemical Laboratory has been newly equipped. Every facility is offered to Students desiring to undertake Research work.

POLYTECHNIC INSTITUTE, 309, Regent Street, London, W.—Mr. R. A. Ward and Assistants.—Evening Classes in Theoretical and Practical Chemistry, &c. The Classes are open to both sexes. The next term commences on Monday, September 28th.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C. (Science Department of the Univ. Coll.).—The large Chemical, Biological, and Physical laboratories have been found admirably suited to their purpose, and the proportion of passes in the London University Science Lists has increased rapidly. Students may work either for long or short periods, either for examination or for private practice. The Laboratories accommodate over 100 Students.

WESTMINSTER COLLEGE OF CHEMISTRY AND PHARMACY, Trinity Square, Borough, S.E.—Messrs. Wills and Wootton. Day and Evening Classes.

THE CLIFTON LABORATORY, Berkeley Square, Bristol.—Principal, E. H. Cook, D.Sc. (Lond.), F.I.C. Students are received either as Private Pupils or Members of a Class. Instruction is given to those requiring to use science or scientific methods in Commercial and Industrial pursuits, or in preparing for Examinations. Students are urged to undertake researches and receive special attention from the teachers. Every effort is made to produce thorough chemists rather than successful examinees.

LEEDS SCHOOL OF SCIENCE AND TECHNOLOGY, (Mechanics' Institution, Leeds).—Lecturer on Chemistry, Mr. S. J. Harris, M.Sc. Assistant Lecturer, Mr. R. W. Ferguson, A.R.C.S. Lecturer on Metallurgy, Mr. B. A. Burrell, F.I.C. Lecturer on Physics, Mr. J. E. Tindall, B.Sc. The Chemical Laboratory is open for four evenings, and the Metallurgical Laboratory for two evenings per week. There is a three years' course of lectures in Inorganic Chemistry, and a two years' course in Organic Chemistry and Metallurgy. The laboratory courses in Physics and Chemistry prepare for the final B.Sc. examination at London University.

INSTITUTE OF CHEMICAL TECHNOLOGY, Hackins Hey, Liverpool (A. Norman Tate and Co.).—Principal, Mr. F. H. Tate, F.C.S. The course of instruction is intended

more especially for students who wish to gain a knowledge of chemistry and the allied sciences in their relation to industrial and commercial pursuits, and embraces a thorough preliminary course of theoretical chemistry and practical laboratory work, followed by instruction in chemical technology fitted to the requirements of each pupil. In addition to these chemical studies, students who desire it can enter upon a special course calculated to afford them knowledge useful in the erection and arrangement of manufactories and plant, and construction of apparatus.

THE MUNICIPAL TECHNICAL SCHOOL, Princess Street, Manchester.—Theoretical and Practical Chemistry, Mr. E. Knecht, Ph.D., F.I.C., Mr. J. Grant, F.I.C., F.C.S., Mr. L. G. Radcliffe, and Mr. J. Allan. Metallurgy, Mr. E. L. Rhead. At this important Municipal School, with an attendance of upwards of 3000 Students, there are organised Day Courses in Pure Chemistry, with applications to Dyeing, Bleaching, Printing, Brewing, and Metallurgy. In addition there are Evening Courses, not only in Pure Chemistry, but in Metallurgy, Mineralogy, Iron and Steel Manufacture, Brewing, Bleaching, Dyeing, and Printing, Coal Tar Products, Paper Manufacture, Gas Analysis, Pharmaceutical Preparations, Chemical Engineering, Chemistry for Engineers and Builders, and Photography. The complete Syllabus (4d., by post 6d.) may be obtained on application to Mr. J. H. Reynolds, Director and Secretary, Princess Street, Manchester.

HIGHER GRADE SCHOOL, PATRICROFT.—Science and Art Day and Evening School, and Institute for Women. Demonstrator in Chemistry, Mr. R. J. B. Sanderson.

TECHNICAL INSTITUTE, BIRLEY STREET, BESWICK.—Demonstrator in Chemistry, Mr. R. J. B. Sanderson.

SHEFFIELD BOROUGH ANALYSTS' LABORATORY, 1, Surrey Street.—Mr. A. H. Allen, F.C.S. Day and Evening Classes.

STOCKPORT TECHNICAL SCHOOL.—Department of Chemistry and Dyeing.—Principal: Mr. R. J. Brown, M.Sc. A syllabus with full particulars of the courses of instruction, hours, fees, &c., is obtainable on application. Special instruction is given in the Dyeing of Felt, &c., as applied to Hat Manufacture.

TECHNICAL INSTITUTE, SWANSEA.—Classes in Theoretical and Practical Organic and Inorganic Chemistry, Metallurgy, Hygiene, Mathematics, Physiology, Sound, Light, and Heat, from October to May. Principals, D. J. Morgan, B.A. (Cantab.), C. A. Seyler, B.Sc., F.I.C.

ABERDEEN UNIVERSITY.—Prof. Japp.

SCHOOL OF MEDICINE, Edinburgh.—Dr. S. Macadam, Mr. King, Mr. I. Macadam, and Drs. Aitken and Readman.

ST. MUNGO'S COLLEGE AND SCHOOL OF MEDICINE, EDINBURGH.—Dr. Marshall.

SURGEON'S HALL, Nicolson Street, Edinburgh.—Mr. Ivison Macadam. Laboratory work and demonstrations in Agricultural Chemistry. Chemistry Class for Women.

GLASGOW UNIVERSITY.—Prof. J. Ferguson.

GLASGOW VETERINARY COLLEGE.—Professor, T. L. Goodwin, Systematic Course, Oct. 6 to May 9. Laboratory daily, except Saturdays, for private students. Saturday class for teachers, 9 to 1.

ANDERSON'S COLLEGE, GLASGOW.—Mr. J. R. Watson.

ROYAL COLLEGE OF SURGEONS IN IRELAND, DUBLIN.—Professor of Chemistry and Hygiene: Sir Charles A. Cameron, M.D., F.R.C.S.I. Instruction is given in the College Laboratory in General, Practical, and Analytical Chemistry, and in the subjects (Physical, Chemical, and Microscopical) required for Examinations in Public Health and to educate for the position of Public Analyst.

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UNIVERSITY COLLEGE, NOTTINGHAM.

SESSION 1896-97.

The SESSION begins SEPTEMBER 28th.

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1921.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

LIVERPOOL, 1896.

INAUGURAL ADDRESS OF THE PRESIDENT, SIR JOSEPH LISTER, BART., D.C.L., LL.D., F.R.S.

My Lord Mayor, my Lords, Ladies, and Gentlemen, I have first to express my deep sense of gratitude for the great honour conferred upon me by my election to the high office which I occupy to-day. It came upon me as a great surprise. The engrossing claims of surgery have prevented me for many years from attending the meetings of the Association, which excludes from her sections medicine in all its branches. This severance of the art of healing from the work of the Association was right and indeed inevitable. Not that medicine has little in common with science. The surgeon never performs an operation without the aid of anatomy and physiology; and in what is often the most difficult part of his duty, the selection of the right course to follow, he, like the physician, is guided by pathology, the science of the nature of disease, which, though very difficult from the complexity of its subject matter, has made during the last half-century astonishing progress; so that the practice of medicine in every department is becoming more and more based on science as distinguished from empiricism. I propose on the present occasion to bring before you some illustrations of the interdependence of science and the healing art; and the first that I will take is perhaps the most astonishing of all results of purely physical inquiry—the discovery of the Röntgen rays, so called after the man who first clearly revealed them to the world. Mysterious as they still are, there is one of their properties which we can all appreciate—their power of passing through substances opaque to ordinary light. There seems to be no relation whatever between transparency in the common sense of the term and penetrability to these emanations. The glasses of a pair of spectacles may arrest them, while their wooden and leathern case allows them to pass almost unchecked. Yet they produce, whether directly or indirectly, the same effects as light upon a photographic plate. As a general rule the denser any object is the greater obstacle does it oppose to the rays. Hence, as bone is denser than flesh, if the hand or other part of the body is placed above the sensitive film enclosed in a case of wood or other light material at a suitable distance from the source of the rays, while they pass with the utmost facility through the uncovered parts of the lid of the box and powerfully affect the plate beneath, they are arrested to a large extent by the bones, so that the plate is little acted upon in the parts opposite to them, while the portions corresponding to the muscles and other soft parts are influenced in an intermediate degree. Thus a picture is obtained in which the bones stand out in sharp relief among the flesh, and anything abnormal in their shape or position is clearly displayed.

I need hardly point out what important aid this must give to the surgeon. As an instance, I may mention a case which occurred in the practice of Mr. Howard Marsh. He was called to see a severe injury of the elbow, in which the swelling was so great as to make it impossible for him by ordinary means of examination to decide whether he had to deal with a fracture or a disloca-

tion. If it were the latter, a cure would be effected by the exercise of violence, which would be not only useless but most injurious if a bone was broken. By the aid of the Röntgen rays a photograph was taken, in which the bone of the upper arm was clearly seen displaced forwards on those of the forearm. The diagnosis being thus established, Mr. Marsh proceeded to reduce the dislocation; and his success was proved by another photograph which showed the bones in their natural relative position.

The common metals, such as lead, iron, and copper, being still denser than the osseous structures, these rays can show a bullet embedded in a bone or a needle lodged about a joint. At the last conversazione of the Royal Society, a picture produced by the new photography displayed with perfect distinctness through the bony framework of the chest a halfpenny low down in a boy's gullet. It had been there for six months, causing uneasiness at the pit of the stomach during swallowing; but whether the coin really remained impacted, or if so, what was its position, was entirely uncertain till the Röntgen rays revealed it. Dr. Macintyre, of Glasgow, who was the photographer, informs me that when the presence of the halfpenny had been thus demonstrated, the surgeon in charge of the case made an attempt to extract it, and, although this was not successful in its immediate object, it had the effect of dislodging the coin, for a subsequent photograph by Dr. Macintyre not only showed that it had disappeared from the gullet, but also, thanks to the wonderful penetrating power which the rays had acquired in his hands, proved that it had not lodged further down in the alimentary passage. The boy has since completely recovered.

The Röntgen rays cause certain chemical compounds to fluoresce, and emit a faint light plainly visible in the dark; and if they are made to fall upon a translucent screen impregnated with such a salt, it becomes beautifully illuminated. If a part of the human body is interposed between the screen and the source of the rays, the bones and other structures are thrown in shadow upon it, and thus a diagnosis can be made without the delay involved in taking a photograph. It was in fact in this way that Dr. Macintyre first detected the coin in the boy's gullet. Mr. Herbert Jackson, of King's College, London, early distinguished himself in this branch of the subject. There is no reason to suppose that the limits of the capabilities of the rays in this way have yet been reached. By virtue of the greater density of the heart than the adjacent lungs with their contained air, the form and dimensions of that organ in the living body may be displayed on the fluorescent screen, and even its movements have been lately seen by several different observers.

Such important applications of the new rays to medical practice have strongly attracted the interest of the public to them, and I venture to think that they have even served to stimulate the investigations of physicists. The eminent Professor of Physics in the University College of this city (Professor Lodge) was one of the first to make such practical applications, and I was able to show to the Royal Society at a very early period a photograph, which he had the kindness to send me, of a bullet embedded in the hand. His interest in the medical aspect of the subject remains unabated, and at the same time he has been one of the most distinguished investigators of its purely physical side.

There is another way in which the Röntgen rays connect themselves with physiology, and may possibly influence medicine. It is found that if the skin is long exposed to their action it becomes very much irritated, affected with a sort of aggravated sun-burning. This suggests the idea that the transmission of the rays through the human body may be not altogether a matter of indifference to internal organs, but may, by long-continued action, produce, according to the condition of the part concerned, injurious irritation or salutary stimulation.

This is the jubilee of Anæsthesia in surgery. That priceless blessing to mankind came from America. It had, indeed, been foreshadowed in the first year of this century by Sir Humphry Davy, who, having found a toothache from which he was suffering relieved as he inhaled laughing gas (nitrous oxide), threw out the suggestion that it might perhaps be used for preventing pain in surgical operations. But it was not till, on September 30, 1846, Dr. W. T. G. Morton, of Boston, after a series of experiments upon himself and the lower animals, extracted a tooth painlessly from a patient whom he had caused to inhale the vapour of sulphuric ether, that the idea was fully realised. He soon afterwards publicly exhibited his method at the Massachusetts General Hospital, and after that event the great discovery spread rapidly over the civilised world. I witnessed the first operation in England under ether. It was performed by Robert Liston in University College Hospital, and it was a complete success. Soon afterwards I saw the same great surgeon amputate the thigh as painlessly, with less complicated anæsthetic apparatus, by aid of another agent, chloroform, which was being powerfully advocated as a substitute for ether by Dr. (afterwards Sir James Y.) Simpson, who also had the great merit of showing that confinements could be conducted painlessly, yet safely, under its influence. These two agents still hold the field as general anæsthetics for protracted operations, although the gas originally suggested by Davy, in consequence of its rapid action and other advantages, has taken their place in short operations, such as tooth extraction. In the birthplace of anæsthesia ether has always maintained its ground; but in Europe it was to a large extent displaced by chloroform till recently, when many have returned to ether, under the idea that, though less convenient, it is safer. For my own part, I believe that chloroform, if carefully administered on right principles, is, on the average, the safer agent of the two.

The discovery of anæsthesia inaugurated a new era in surgery. Not only was the pain of operations abolished, but the serious and sometimes mortal shock which they occasioned to the system was averted, while the patient was saved the terrible ordeal of preparing to endure them. At the same time the field of surgery became widely extended, since many procedures in themselves desirable, but before impossible from the protracted agony they would occasion, became matters of routine practice. Nor have I by any means exhausted the list of the benefits conferred by this discovery.

Anæsthesia in surgery has been from first to last a gift of science. Nitrous oxide, sulphuric ether, and chloroform are all artificial products of chemistry, their employment as anæsthetics was the result of scientific investigation, and their administration, far from being, like the giving of a dose of medicine, a matter of rule-of-thumb, imperatively demands the vigilant exercise of physiological and pathological knowledge.

While rendering such signal service to surgery, anæsthetics have thrown light upon biology generally. It has been found that they exert their soporific influence not only upon Vertebrata, but upon animals so remote in structure from man as bees and other insects. Even the functions of vegetables are suspended by their agency. They thus afford strong confirmation of the great generalisation that living matter is of the same essential nature wherever it is met with on this planet, whether in the animal or vegetable kingdom. Anæsthetics have also, in ways to which I need not here refer, powerfully promoted the progress of physiology and pathology.

My next illustration may be taken from the work of Pasteur on fermentation. The prevailing opinion regarding this class of phenomena when they first engaged his attention was that they were occasioned primarily by the oxygen of the air acting upon unstable animal or vegetable products, which, breaking up under its influence, communicated disturbance to other organic materials in their vicinity, and thus led to their decomposition.

Cagniard-Latour had indeed shown several years before that yeast consists essentially of the cells of a microscopic fungus which grows as the sweetwort ferments; and he had attributed the breaking up of the sugar into alcohol and carbonic acid to the growth of the micro-organism. In Germany, Schwann, who independently discovered the yeast plant, had published very striking experiments in support of analogous ideas regarding the putrefaction of meat. Such views had also found other advocates, but they had become utterly discredited, largely through the great authority of Liebig, who bitterly opposed them.

Pasteur, having been appointed as a young man Dean of the Faculty of Sciences in the University of Lille, a town where the products of alcoholic fermentation were staple articles of manufacture, determined to study that process thoroughly; and as a result he became firmly convinced of the correctness of Cagniard-Latour's views regarding it. In the case of other fermentations, however, nothing fairly comparable to the formation of yeast had till then been observed. This was now done by Pasteur for that fermentation in which sugar is resolved into lactic acid. This lactic fermentation was at that time brought about by adding some animal substance, such as fibrin, to a solution of sugar, together with chalk, that should combine with the acid as it was formed. Pasteur saw, what had never before been noticed, that a fine grey deposit was formed, differing little in appearance from the decomposing fibrin, but steadily increasing as the fermentation proceeded. Struck by the analogy presented by the increasing deposit to the growth of yeast in sweetwort, he examined it with the microscope, and found it to consist of minute particles of uniform size. Pasteur was not a biologist, but although these particles were of extreme minuteness in comparison with the constituents of the yeast plant, he felt convinced that they were of an analogous nature, the cells of a tiny microscopic fungus. This he regarded as the essential ferment, the fibrin or other so-called ferment serving, as he believed, merely the purpose of supplying to the growing plant certain chemical ingredients not contained in the sugar, but essential to its nutrition. And the correctness of this view he confirmed in a very striking manner, by doing away with the fibrin or other animal material altogether, and substituting for it mineral salts containing the requisite chemical elements. A trace of the grey deposit being applied to a solution of sugar containing these salts in addition to the chalk, a brisker lactic fermentation ensued than could be procured in the ordinary way.

I have referred to this research in some detail because it illustrates Pasteur's acuteness as an observer and his ingenuity in experiment, as well as his almost intuitive perception of truth.

A series of other beautiful investigations followed, clearly proving that all true fermentations, including putrefaction, are caused by the growth of micro-organisms.

It was natural that Pasteur should desire to know how the microbes, which he showed to be the essential causes of the various fermentations, took their origin. It was at that period a prevalent notion, even among many eminent naturalists, that such humble and minute beings originated *de novo* in decomposing organic substances; the doctrine of spontaneous generation, which had been chased successively from various positions which it once occupied among creatures visible to the naked eye, having taken its last refuge where the objects of study were of such minuteness that their habits and history were correspondingly difficult to trace. Here again Pasteur at once saw, as if by instinct, on which side the truth lay; and, perceiving its immense importance, he threw himself with ardour into its demonstration. I may describe briefly one class of experiments which he performed with this object. He charged a series of narrow-necked glass flasks with a decoction of yeast, a liquid peculiarly liable to alteration on exposure to the air. Having boiled the liquid in each

flask, to kill any living germs it might contain, he sealed its neck with a blowpipe during ebullition; after which, the flask being allowed to cool, the steam within it condensed, leaving a vacuum above the liquid. If, then, the neck of the flask were broken in any locality, the air at that particular place would rush in to fill the vacuum, carrying with it any living microbes that might be floating in it. The neck of the flask having been again sealed, any germs so introduced would in due time manifest their presence by developing in the clear liquid. When any of such a series of flasks were opened and re-sealed in an inhabited room, or under the trees of a forest, multitudes of minute living forms made their appearance in them; but if this was done in a cellar long unused, where the suspended organisms, like other dust, might be expected to have all fallen to the ground, the decoction remained perfectly clear and unaltered. The oxygen and other gaseous constituents of the atmosphere were thus shown to be of themselves incapable of inducing any organic development in yeast-water.

Such is a sample of the many well-devised experiments by which he carried to most minds the conviction that, as he expressed it, "*la génération spontanée est une chimère*," and that the humblest and minutest living organisms can only originate by parentage from beings like themselves.

Pasteur pointed out the enormous importance of these humble organisms in the economy of Nature. It is by their agency that the dead bodies of plants and animals are resolved into simpler compounds fitted for assimilation by new living forms. Without their aid the world would be, as Pasteur expresses it, *encombré de cadavres*. They are essential not only to our well-being, but to our very existence. Similar microbes must have discharged the same necessary function of removing refuse and providing food for successive generations of plants and animals during the past periods of the world's history; and it is interesting to think that organisms as simple as can well be conceived to have existed when life first appeared upon our globe have, in all probability, propagated the same lowly but most useful offspring during the ages of geological time.

Pasteur's labours on fermentation have had a very important influence upon surgery. I have been often asked to speak on my share in this matter before a public audience; but I have hitherto refused to do so, partly because the details are so entirely technical, but chiefly because I have felt an invincible repugnance to what might seem to savour of self-advertisement. The latter objection now no longer exists, since advancing years have indicated that it is right for me to leave to younger men the practice of my dearly loved profession. And it will perhaps be expected that, if I can make myself intelligible, I should say something upon the subject on the present occasion.

Nothing was formerly more striking in surgical experience than the difference in the behaviour of injuries according to whether the skin was implicated or not. Thus, if the bones of the leg were broken and the skin remained intact, the surgeon applied the necessary apparatus without any other anxiety than that of maintaining a good position of the fragments, although the internal injury to bones and soft parts might be very severe. If, on the other hand, a wound of the skin was present communicating with the broken bones, although the damage might be in other respects comparatively slight, the compound fracture, as it was termed, was one of the most dangerous accidents that could happen. Mr. Syme, who was, I believe, the safest surgeon of his time, once told me that he was inclined to think that it would be, on the whole, better if all compound fractures of the leg were subjected to amputation, without any attempt to save the limb. What was the cause of this astonishing difference? It was clearly in some way due to the exposure of the injured parts to the external world. One obvious effect of such exposure was indicated by the odour of the discharge, which showed that the blood in the wound

had undergone putrefactive change by which the bland nutrient liquid had been converted into highly irritating and poisonous substances. I have seen a man with compound fracture of the leg die within two days of the accident, as plainly poisoned by the products of putrefaction as if he had taken a fatal dose of some potent toxic drug.

An external wound of the soft parts might be healed in one of two ways. If its surfaces were clean cut and could be brought into accurate apposition, it might unite rapidly and painlessly "by the first intention." This, however, was exceptional. Too often the surgeon's efforts to obtain primary union were frustrated; the wound inflamed and the retentive stitches had to be removed, allowing it to gape; and then, as if it had been left open from the first, healing had to be effected in the other way which it is necessary for me briefly to describe. An exposed raw surface became covered in the first instance with a layer of clotted blood or certain of its constituents, which invariably putrefied; and the irritation of the sensitive tissues by the putrid products appeared to me to account sufficiently for the inflammation which always occurred in and around an open wound during the three or four days which elapsed before what were termed "granulations" had been produced. These constituted a coarsely granular coating of very imperfect or embryonic structure, destitute of sensory nerves and prone to throw off matter or pus, rather than absorb, as freshly divided tissues do, the products of putrefaction. The granulations thus formed a beautiful living plaster, which protected the sensitive parts beneath from irritation, and the system generally from poisoning and consequent febrile disturbance. The granulations had other useful properties, of which I may mention their tendency to shrink as they grew, thus gradually reducing the dimensions of the sore. Meanwhile another cause of its diminution was in operation. The cells of the epidermis or scarf-skin of the cutaneous margins were perpetually producing a crop of young cells of similar nature, which gradually spread over the granulations till they covered them entirely, and a complete cicatrix or scar was the result. Such was the other mode of healing, that by granulation and cicatrization; a process which, when it proceeded unchecked to its completion, commanded our profound admiration. It was, however, essentially tedious compared with primary union, while, as we have seen, it was always preceded by more or less inflammation and fever, sometimes very serious in their effects. It was also liable to unforeseen interruptions. The sore might become larger instead of smaller, cicatrization giving place to ulceration in one of its various forms, or even to the frightful destruction of tissue which, from the circumstance that it was most frequently met with in hospitals, was termed hospital gangrene. Other serious and often fatal complications might arise, which the surgeon could only regard as untoward accidents and over which he had no efficient control.

It will be readily understood from the above description that the inflammation which so often frustrated the surgeon's endeavours after primary union was in my opinion essentially due to decomposition of blood within the wound.

These and many other considerations had long impressed me with the greatness of the evil of putrefaction in surgery. I had done my best to mitigate it by scrupulous ordinary cleanliness and the use of various deodorant lotions. But to prevent it altogether appeared hopeless while we believed with Liebig that its primary cause was the atmospheric oxygen which, in accordance with the researches of Graham, could not fail to be perpetually diffused through the porous dressings which were used to absorb the blood discharged from the wound. But when Pasteur had shown that putrefaction was a fermentation caused by the growth of microbes, and that these could not arise *de novo* in the decomposable substance, the problem assumed a more hopeful aspect. If the wound could be treated with some substance which, without doing, too

serious mischief to the human tissues, would kill the microbes already contained in it and prevent the future access of others in the living state, putrefaction might be prevented, however freely the air with its oxygen might enter. I had heard of carbolic acid as having a remarkable deodorising effect upon sewage, and having obtained from my colleague, Dr. Anderson, Professor of Chemistry in the University of Glasgow, a sample which he had of this product, then little more than a chemical curiosity in Scotland, I determined to try it in compound fractures. Applying it undiluted to the wound, with an arrangement for its occasional renewal, I had the joy of seeing these formidable injuries follow the same safe and tranquil course as simple fractures, in which the skin remains unbroken.

At the same time we had the intense interest of observing in open wounds what had previously been hidden from human view, the manner in which subcutaneous injuries are repaired. Of special interest was the process by which portions of tissue killed by the violence of the accident were disposed of, as contrasted with what had till then been invariably witnessed. Dead parts had been always seen to be gradually separated from the living by an inflammatory process and thrown off as sloughs. But when protected by the antiseptic dressing from becoming putrid and therefore irritating, a structure deprived of its life caused no disturbance in its vicinity; and, on the contrary, being of a nutritious nature, it served as pabulum for the growing elements of the neighbouring living structures, and these became in due time entirely substituted for it. Even dead bone was seen to be thus replaced by living osseous tissue.

This suggested the idea of using threads of dead animal tissue for tying blood vessels; and this was realised by means of catgut, which is made from the intestine of the sheep. If deprived of living microbes, and otherwise properly prepared, catgut answers its purpose completely; the knot holding securely, while the ligature around the vessel becomes gradually absorbed and replaced by a ring of living tissue. The threads, instead of being left long as before, could now be cut short, and the tedious process of separation of the ligature, with its attendant serious danger of bleeding, was avoided.

Undiluted carbolic acid is a powerful caustic; and although it might be employed in compound fracture, where some loss of tissue was of little moment in comparison with the tremendous danger to be averted, it was altogether unsuitable for wounds made by the surgeon. It soon appeared, however, that the acid would answer the purpose aimed at, though used in diluted forms devoid of caustic action, and therefore applicable to operative surgery. According to our then existing knowledge, two essential points had to be aimed at: to conduct the operation so that on its completion the wound should contain no living microbes, and to apply a dressing capable of preventing the access of other living organisms till the time should have arrived for changing it.

Carbolic acid lent itself well to both these objects. Our experience with this agent brought out what was, I believe, a new principle in pharmacology—namely, that the energy of action of any substance upon the human tissues depends not only upon the proportion in which it is contained in the material used as a vehicle for its administration, but also upon the degree of tenacity with which it is held by its solvent. Water dissolves carbolic acid sparingly and holds it extremely lightly, leaving it free to act energetically on other things for which it has greater affinity, while various organic substances absorb it greedily and hold it tenaciously. Hence its watery solution seemed admirably suited for a deterrent lotion to be used during the operation for destroying any microbes that might fall upon the wound, and for purifying the surrounding skin and also the surgeon's hands and instruments. For the last-named purpose it had the further advantage that it did not act on steel.

For an external dressing the watery solution was not adapted, as it soon lost the acid it contained, and was

irritating while it lasted. For this purpose some organic substances were found to answer well. Large proportions of the acid could be blended with them in so bland a form as to be unirritating; and such mixtures, while perpetually giving off enough of the volatile salt to prevent organic development in the discharges that flowed past them, served as a reliable store of the antiseptic for days together.

The appliances which I first used for carrying out the antiseptic principle were both rude and needlessly complicated. The years that have since passed have witnessed great improvements in both respects. Of the various materials which have been employed by myself and others, and their modes of application, I need say nothing except to express my belief, as a matter of long experience, that carbolic acid, by virtue of its powerful affinity for the epidermis and oily matters associated with it, and also its great penetrating power, is still the best agent at our disposal for purifying the skin around the wound. But I must say a few words regarding a most important simplification of our procedure. Pasteur, as we have seen, had shown that the air of every inhabited room teems with microbes; and for a long time I employed various more or less elaborate precautions against the living atmospheric dust, not doubting that, as all wounds except the few which healed completely by the first intention underwent putrefactive fermentation, the blood must be a peculiarly favourable soil for the growth of putrefactive microbes. But I afterwards learnt that such was by no means the case. I had performed many experiments in confirmation of Pasteur's germ theory, not indeed in order to satisfy myself of its truth, but in the hope of convincing others. I had observed that uncontaminated milk, which would remain unaltered for an indefinite time if protected from dust, was made to teem with microbes of very different kinds by a very brief exposure to the atmosphere, and that the same effect was produced by the addition of a drop of ordinary water. But when I came to experiment with blood drawn with antiseptic precautions into sterilised vessels, I saw to my surprise that it might remain free from microbes in spite of similar access of air or treatment with water. I even found that if very putrid blood was largely diluted with sterilised water, so as to diffuse its microbes widely and wash them of their acid products, a drop of such dilution added to pure blood might leave it unchanged for days at the temperature of the body, although a trace of the septic liquid undiluted caused intense putrefaction within twenty-four hours. Hence I was led to conclude that it was the grosser forms of septic mischief, rather than microbes in the attenuated condition in which they existed in the atmosphere, that we had to dread in surgical practice. And at the London Medical Congress in 1881, I hinted, when describing the experiments I have alluded to, that it might turn out possible to disregard altogether the atmospheric dust. But greatly as I should have rejoiced at such a simplification of our procedure, if justifiable, I did not then venture to test it in practice. I knew that with the safeguards which we then employed I could ensure the safety of my patients, and I did not dare to imperil it by relaxing them. There is one golden rule for all experiments upon our fellow-men: Let the thing tried be that which, according to our best judgment, is the most likely to promote the welfare of the patient. In other words, Do as you would be done by.

Nine years later, however, at the Berlin Congress in 1890, I was able to bring forward what was, I believe, absolute demonstration of the harmlessness of the atmospheric dust in surgical operations. This conclusion has been justified by subsequent experience; the irritation of the wound by antiseptic irrigation and washing may therefore now be avoided, and nature left quite undisturbed to carry out her best methods of repair, while the surgeon may conduct his operations as simply as in former days, provided always that, deeply impressed with the tremendous importance of his object, and inspiring the

same conviction in all his assistants, he vigilantly maintains from first to last, with a care that, once learnt, becomes instinctive, but for the want of which nothing else can compensate, the use of the simple means which will suffice to exclude from the wound the coarser forms of septic impurity.

Even our earlier and ruder methods of carrying out the antiseptic principle soon produced a wonderful change in my surgical wards in the Glasgow Royal Infirmary, which, from being some of the most unhealthy in the kingdom, became, as I believe I may say without exaggeration, the healthiest in the world; while other wards, separated from mine only by a passage of a few feet broad, where former modes of treatment were for a while continued, retained their former insalubrity. This result, I need hardly remark, was not in any degree due to special skill on my part, but simply to the strenuous endeavour to carry out strictly what seemed to me a principle of supreme importance.

Equally striking changes were afterwards witnessed in other institutions. Of these I may give one example. In the great Allgemeines Krankenhaus of Munich, hospital gangrene had become more and more rife from year to year, till at length the frightful condition was reached that 80 per cent of all wounds became affected by it. It is only just to the memory of Professor von Nussbaum, then the head of that establishment, to say that he had done his utmost to check this frightful scourge; and that the evil was not caused by anything peculiar in his management was shown by the fact that in a private hospital under his care there was no unusual unhealthiness. The larger institution seemed to have become hopelessly infected, and the city authorities were contemplating its demolition and re-construction. Under these circumstances, Professor von Nussbaum despatched his chief assistant, Dr. Lindpaintner, to Edinburgh, where I at that time occupied the chair of clinical surgery, to learn the details of the antiseptic system, as we then practised it. He remained until he had entirely mastered them, and after his return all the cases were on a certain day dressed on our plan. From that day forward not a single case of hospital gangrene occurred in the Krankenhaus. The fearful disease pyæmia likewise disappeared, and erysipelas soon followed its example.

But it was by no means only in removing the unhealthiness of hospitals that the antiseptic system showed its benefits. Inflammation being suppressed, with attendant pain, fever, and wasting discharge, the sufferings of the patient were, of course, immensely lessened; rapid primary union being now the rule, convalescence was correspondingly curtailed; while as regards safety and the essential nature of the mode of repair, it became a matter of indifference whether the wound had clean-cut surfaces which could be closely approximated, or whether the injury inflicted had been such as to cause destruction of tissue. And operations which had been regarded from time immemorial as unjustifiable were adopted with complete safety.

It pleases me to think that there is an ever-increasing number of practitioners throughout the world to whom this will not appear the language of exaggeration. There are cases in which, from the situation of the part concerned or other unusual circumstances, it is impossible to carry out the antiseptic system completely. These, however, are quite exceptional; and even in them much has been done to mitigate the evil which cannot be altogether avoided.

(To be continued).

Tea Cigarettes.—According to the *Indian Pharmacologist*, the demand for tea in India and Ceylon has been stimulated by a new demand which has sprung up in America for its use as a substitute for tobacco in the manufacture of cigarettes. Their use is said to be more deleterious than that of opium. Will a society be formed to agitate for the prohibition of the culture of tea?

THE INTRODUCTION OF STANDARD METHODS OF ANALYSIS.*

By the Baron HANNS JÜPTNER VON JONSTORFF
(Neuberg, Austria).

(Continued from p. 118).

7. *Errors caused by Differences in the Calculation of the Analyses based on the Atomic Weights.*—During recent years a series of revisions of the values of the atomic weights have been published, but unfortunately they do not in all cases present the desired agreement among themselves. As, in cases where the greatest possible accuracy is required, it appears only natural to employ these revised values in the calculation of the analyses, it may not be superfluous to discuss them in detail.

The oldest of these new determination is that of F. W. Clarke ("Constants of Nature," 1882). This was followed in 1883 by the work on the "Atomic Weights of the Elements," by L. Meyer and K. Seubert, whose statements, like the previous ones of Clarke, have found the widest circulation in technical circles. In 1886, Van der Plaats (*Ann. de Chim. et de Phys.*, Series 6, vol. vii., April) published the results of his new determinations, and, lastly, in 1893, F. W. Clarke (*Journal of the American Chemical Society*, vol. xvi., p. 179; *Chemisches Centralblatt*, 1894, No. 1, p. 810) undertook a revision of the values of the atomic weights previously published by him. As the last values have not yet been generally adopted, his older results must here also be taken into account. The atomic weights of the elements of greatest importance in the iron and steel industries, as set forth in the works cited are as follows:—

Element.	F. W. Clarke. 1882.	L. Meyer and K. Seubert.		Van der Plaats.		Clarke. 1893.
		Atomic weight.	Possible error.	Atomic weight.	Possible error.	
Chromium ..	52.009	52.45	0.5-1.0	52.3	0.3	52.1
Iron ..	55.913	55.88	0.1	56.0	0.05	56.0
Magnesium .	23.959	23.94	0.5-1.0	24.4	0.05	24.3
Manganese .	53.906	54.80	0.5-1.0	55.0	0.1	55.0
Phosphorus .	30.958	30.96	0.1	30.95	0.05	31.0
Oxygen ..	15.9633	15.96	>0.5	16.0	—	16.0
Sulphur ..	31.984	31.98	>0.5	32.06	0.01	32.06
Silicon ..	28.195	28.00	0.5-1.0	28.0	0.1	28.4
Barium ..	137.763	136.86	0.5	137.1	0.1	137.43

From this the figures given in table (see next page) are calculated for some of the more important compounds.

If, in the titration of manganese (by the chlorate method), with ferrous ammonium sulphate and permanganate, the manganese value of the permanganate standard is calculated from its iron value, one atom of manganese corresponds with two atoms of iron. The corresponding atomic weights are then as follows:—

	Iron.	Manganese.
Clarke, 1882	55.913	53.906
L. Meyer and K. Seubert..	55.88	54.8
Van der Plaats.. .. .	56.0	55.0
Clarke, 1893	56.0	55.0

Thus, one part by weight of iron represents—

According to—	Parts by weight of Manganese.
Clarke, 1882.. .. .	0.48205
L. Meyer and K. Seubert ..	0.49033
Van der Plaats	0.49107
Clarke, 1893.. .. .	0.49107

The maximum difference is—

$$\Delta_3 - 1 = 1.87 \text{ per cent.}$$

$$\Delta_4 - 2 = 0.15 \text{ per cent.}$$

* Read before the Iron and Steel Institute.

Compound.	Clarke, 1882.	L. Meyer and K. Seubert.	Van der Plaats.	Clarke, 1893.	Maximum difference, per cent.
Ferric oxide, Fe_2O_3 .	Fe_2 O_3	111'826 47'8899	111'76 47'28	112'0 48'0	112'0 48'0
	Fe_2O_3	159'7159	159'64	160'0	160'0
	1 pt. by wt. Fe_2O_3 = pt. by wt. Fe	0'70016	0'70008	0'70000	0'7000
					$\Delta_1 - 3 = 0'02$ $\Delta_2 - 4 = 0'01$
	S O_4 Ba	31'984 63'8532 136'763	31'98 63'84 136'86	32'06 64'00 137'10	32'06 64'00 137'43
Barium sulphate BaSO_4 .	BaSO_4	232'6002	232'68	233'16	233'49
	1 pt. by wt. BaSO_4 = pt. by wt. S	0'13750	0'13744	0'13750	0'13730
					$\Delta_1 - 2 = 0'04$ $\Delta_3 - 4 = 0'14$
	1 pt. by wt. BaSO_4 = pt. by wt. Ba	0'58797	0'58819	0'58801	0'58859
					$\Delta_2 - 1 = 0'04$ $\Delta_4 - 3 = 0'10$
Magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$.	Mg_2 P_2 O_7	47'918 61'916 111'7431	47'88 61'92 111'72	48'8 61'9 112'0	48'6 62'0 112'0
	$\text{Mg}_2\text{P}_2\text{O}_7$	221'5771	221'52	222'7	222'6
	1 pt. by wt. $\text{Mg}_2\text{P}_2\text{O}_7$ = pt. by wt. Mg	0'21626	0'21601	0'21913	0'21833
					$\Delta_3 - 2 = 1'44$
	Cr_2 O_3	104'018 47'8899	104'90 47'88	104'60 48'00	104'2 48'0
Chromium oxide, Cr_2O_3 .	Cr_2O_3	151'9079	152'78	152'60	152'2
	1 pt. by wt. Cr_2O_3 = pt. by wt. Cr	0'68474	0'68661	0'68545	0'68462
					$\Delta_2 - 4 = 0'31$
Silica, SiO_2 .	Si O_2	28'195 31'9266	28'0 31'92	28'0 32'0	28'4 32'0
	SiO_2	60'1216	59'92	60'0	60'4
	1 pt. by wt. SiO_2 = pt. by wt. Si	0'46897	0'46729	0'46667	0'47019
					$\Delta_4 - 3 = 0'73$

(a) This difference is 0'4 per cent with pure magnesite, with burnt magnesite it amounts to 1'12 per cent.

(b) Difference with a 50 per cent ferrochrome = 0'15 per cent.

(c) Difference with a 14 per cent ferro-silicon = 0'10 per cent, but with pure quartz = 0'73 per cent.

or, with an 80 per cent ferromanganese, 1'5 or 0'12 per cent.

The atomic weights cited above demand attention, however, from another point of view. For example, L. Meyer and K. Seubert give the possible error in the atomic weights of chromium, magnesium, and silicon as 0'5 to 1'0; this means that analyses, in respect of these elements, may possibly be incorrect to the extent of 50/52 to 100/52, 50/24 to 100/24, and 50/28 to 100/28, or about 1 to 2 per cent, 2 to 4 per cent, and 1½ to 3 per cent respectively. It is evident, therefore, that a thorough revision of the atomic weights in question is urgently needed.

(To be continued).

AN IMPROVED METHOD FOR THE MANUFACTURE OF PEROXIDE OF LEAD.

By H. N. WARREN, Principal Liverpool Research Laboratory.

VARIOUS methods have been devised for the preparation of the above compound, which is now largely consumed in commercial quarters. But hitherto each process presents drawbacks either in one direction or the other. An analytical method of long standing, namely, the action

that nitric acid affords when brought into contact with the red lead of commerce, yields a pure oxide, yet at the same time, besides being costly, it also produces by-products. Again, on the other hand, the use of alkaline hypochlorites produces an oxide contaminated more or less with chlorinated compounds, which adhere with the utmost tenacity.

Several patents have also been claimed for the production of peroxide by dry oxidation, but all more or less yield an impure compound, or present difficulties in controlling the temperature. Taking into account the various difficulties thus set forth, the author, after a varied experience with the above product, recommends the following synthetical mode, which, besides being perfectly under control, possesses the advantage of offering a pure and theoretical yield, free from secondary products:—

In order to bring about the reaction, either litharge or sulphate of lead from vitriol tanks, &c., is introduced into canvas bags, through which is inserted a lead sheet. These bags are now immersed in dilute vitriol, and connected respectively to sheets of iron; the sulphate or other plumbic compound contained therein is thus speedily and completely reduced to the spongy metal, the bags being afterwards connected alternatively by their lead plates and exposed to an electric current, the positives being thus completely converted into peroxide, whilst

the temporary accumulator thus produced is again emptied of its current into further quantities of spongy metal, thus manufacturing a further quantity of peroxide. The process thus set forth, when rightly conducted, yields an absolutely pure oxide, on a cheaper scale than those hitherto recommended.

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SEPARATION OF MERCURY FROM ARSENIC, ANTIMONY, AND COPPER, BY IGNITION IN A CURRENT OF OXYGEN.

By P. JANNASCH.

A. Previous Precipitation by Sulphuretted Hydrogen, and Oxidation of the Filter with Fuming Nitric Acid in Tubulated Apparatus.

1. Separation of Antimony and Mercury.

IN continuation of the separation of mercury and tin effected according to the above method (*Zeitsch. Anorg. Chem.*, xii., p. 132), I have, in concert with H. Heidenreich, succeeded in effecting the separation of mercury from arsenic, antimony, and copper.

The basis of the separation of mercury and antimony is a cautious combustion of the filter freed from the precipitate of sulphide by strong fuming nitric acid (1·4 to 1·5 sp. gr.), and also a complete conversion of antimony sulphide into antimonyl antimoniate. For this purpose the mixture of sulphide, previously collected and washed, is completely dried at 95°; the precipitate is next neatly dissolved away from the filter, which is then set aside in a flat-covered capsule of Meissen porcelain. The empty filter divided in slips is rolled up into rods, thrown into the apparatus, and fuming acid is then gradually added so as to fill about the fourth part of the main tube, and dissolved by agitation and holding the tube in hot water (in a deep capsule), whereon the evaporation of the excess of acid is effected in a current of dry air or carbonic acid over phosphoric acid, for this time only at 90° to 100°. The residue, which has generally a blackish colour, is repeatedly taken up in a similar quantity of nitric acid, and dried as above. After rinsing out the tube with water, the total precipitate, well comminuted with a platinum spatula, is introduced into the apparatus, diffused therein, and moistened with dilute nitric acid, which is simultaneously applied with a washing-bottle for rinsing away any particles which have mechanically adhered to the porcelain.

For the further oxidation of the mixture of sulphides the necessary quantity of ordinary strong nitric acid is dropped in at intervals, and it is again dried over phosphoric acid. The residue is finally further treated twice with the strongest fuming nitric acid in order to complete the oxidation, finally raising the heat each time to 150° to 180°, which especially promotes the completeness of the combustion.

Now follows the ignition in the current of oxygen. The receivers intended to take up the mercury are charged with dilute nitric acid. We ignite at first with a flame of only medium height, proceeding from the front backwards, and finally heating more strongly with the full flame, using at the same time a Bunsen burner to drive over the products of distillation. During such an oxidation of the precipitate not the slightest trace of antimony is sublimed. It is recommended to allow the ignited apparatus to cool very slowly, when the SbO_2 obtained is weighed at once.

In order to secure accurate results the following precautions must be especially observed:—Firstly, the current of oxygen must not be too lively at first, in order that minute particles of antimonyl binoxide may not be mechanically carried along. Further, we must ignite

more strongly at the end, for the complete expulsion of the mercury. In the quantitative cleansing of the main receiver (spiriting out the distillatory tube with hot dilute nitric acid, &c.) we must not overlook minimum particles of metallic mercury, which, on account of their great density, may easily be kept back, and we must pour afterwards into the evaporating capsule 10 to 15 c.c. of hydrogen peroxide. This latter substance exerts a remarkable influence on the solution of the metallic mercury, which at a certain degree of concentration proceeds quite rapidly and smoothly, which is otherwise effected at the end of the concentration only by the joint action of strong nitric and sulphuric acid. It may likewise happen that from the evaporated residue, on the addition of water, a basic salt is deposited, which can be completely re-dissolved only by prolonged heating with dilute hydrochloric acid. If particles of cork have to be filtered off, the washed filter should not be turned by sulphuretted hydrogen water.

The antimony dioxide, weighed direct in the apparatus and absolutely fixed on ignition, has a yellow colour when hot, and when cold white or greyish white. If we wish to withdraw it completely out of the tube, or weigh the antimony as Sb_2S_3 , we fuse it with 8 to 10 parts of sulphur iodide (10 to 15 per cent of iodine) in a current of dry hydrogen sulphide, expel the excess of sulphur, and heat the residual antimony sulphide in a current of bromine.

2. Separation of Mercury from Copper.

About 0·5 grm. copper sulphate and 0·2 grm. mercuric chloride were dissolved in excess of hydrochloric acid diluted to 250 c.c. with warm water, with the addition of 5 c.c. concentrated sulphuric acid, precipitated whilst hot with hydrogen disulphide, filtered, washed, and dried at 95°. The precipitate is separated from the filter, and the latter is incinerated on a weighed tubulated apparatus with oxygen gas, the cuttings of the filter being carefully heated with the free flame.

After complete incineration the whole of the precipitate is added, and heated in a moderate current of oxygen, at first gently and finally strongly, until all the mercury has been driven over. The receivers are filled with dilute nitric acid to which bromine water had been added.

If the copper oxide is to be weighed in the tube, it must be ignited until the weight is constant, keeping in mind the experimental fact that the last traces of sulphuric acid are retained rather obstinately. Oxide of copper thus heated and dissolved in hydrochloric acid gives no reaction for sulphuric acid with a solution of barium chloride; but without igniting to a constant weight, the residual oxide, still occluding traces of sulphuric acid, may be dissolved in a little hot nitric or hydrochloric acid, and this liquid can be precipitated with soda in the known manner.

The liquids in the receivers are rinsed into a porcelain capsule and evaporated almost to dryness, then completely re-dissolved in hydrochloric acid and much water, filtered if needful, and precipitated with hydrogen sulphide whilst hot. The mercury sulphide is weighed upon a filter as usual. We have found it practicable to expel the carbon disulphide (after extraction of the sulphur mixed with precipitate) by means of ether.

B. Ignition of the Mixture Evaporated to Dryness with Acetic Acid and Magnesia.

3. Separation of Arsenic and Mercury in presence of an Excess of Magnesia.

0·3 grm. of mercuric oxide and 0·2 grm. arsenic teroxide (after extra solution of the arsenic in a few drops of soda-lye) are dissolved, at the temperature of the water-bath, by dilute nitric acid, and then dried over phosphoric acid at 120° in a current of air. This mixture is taken up with a few drops of water, 0·6 grm. of pure magnesia (free from chlorine) added, well mixed by shaking up, and again evaporated at the same temperature over phosphoric acid. Finally, it is again heated for about an

hour in a slow current of air to about 180° until all the moisture is expelled. The tube is then lifted out of the phosphoric acid bath, allowed to cool, the outside is cleansed with water, dried, and connected with the oxygen gas-holder and the drying apparatus. It is heated at first very gently with a small flame until the last trace of mercury is removed, afterwards more strongly, and at last with the full flame, in order to drive all the mercury into the receivers which contain dilute nitric acid and 15 c.c. of hydrogen peroxide. After the distillation is completed and the tube cooled, which must be done by gradually screwing down the flame, the fixed residue is dissolved in 5 c.c. concentrated hydrochloric acid, rinsed into a beaker, 3 grms. citric acid added, and finally supersaturated with an excess or strong ammonia. The precipitate of ammonium magnesium arseniate is treated in the known manner, as is also the liquid from the receivers containing all the mercury.—*Zeit. Anorgan. Chem.*, xii., 359.

A NEW METHOD FOR THE ESTIMATION OF IRON OXIDE AND ALUMINA IN PHOSPHATE ROCK.

By THOMAS S. GLADDING.

THE method for the separation of alumina from phosphate of lime by three successive precipitations with ammonium acetate is tedious, though accurate if proper precautions be taken, as shown in a former paper on this subject (*Journ. Am. Chem. Soc.*, xviii., 717; *CHEM. NEWS*, lxxiv., 112).

The following modification suggested itself as saving both time and labour. This modification consists of the separation of alumina from calcium phosphate and iron by means of its solubility in an excess of caustic potash. To demonstrate the accuracy of this method, a solution of ammonia-alum, 20 grms. in a litre, was used as in the previous experiments, 10 c.c. containing 0.0225 gm. Al_2O_3 . The caustic potash solution was made by dissolving 500 grms. of caustic potash in distilled water and diluting to one litre. Chemically pure caustic potash, purified by barium, was used, and was carefully tested for alumina, as much so-called chemically pure potash contains an appreciable amount of alumina.

To a solution of mixed phosphates of alumina, iron, and lime were added 15 c.c. of the C.P. potash solution. The mixture was digested for an hour at a temperature of 70°C ., with occasional stirring. It was then filtered, the filtrate neutralised with hydrochloric acid, and the alumina was precipitated as a phosphate with ammonium acetate, as described in my ammonium acetate method.

Ten c.c. of standard alumina solution + 0.030 gm. iron oxide + 0.500 gm. calcium phosphate gave—

	$\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ found. Grm.	Al_2O_3 . Grm.
1	0.0538	0.0225
2	0.0542	0.0227
3	0.0543	0.0227
4	0.0543	0.0227

Comparative tests were made on phosphate rocks between this method by solution in C.P. potash and by three successive precipitations with ammonium acetate.

	By new potash method. Al_2O_3 found. Per cent.	By acetate method. Al_2O_3 found. Per cent.
1	1.05	1.03
2	1.19	1.16
3	1.86	1.61
4	1.07	0.99
5	1.88	1.98

These results show the accuracy of this method, both in obtaining a known amount of alumina and in showing close agreement with results by the acetate method.

This method has been in use in our laboratory for over a year. A reprint of an article by M. Henri Lasne (*Bull. de la Soc. Chim. de Paris*, [3], xv., 118, 1896) has just been received, giving a method for the separation of alumina from phosphates of iron and lime very similar to this. M. Lasne uses caustic soda instead of potash, and precipitates his aluminum phosphate with ammonium hyposulphite instead of ammonium acetate. I have made a few comparative tests by my method and that of M. Lasne, and find closely-agreeing results.

Using 10 c.c. standard alumina solution + 0.500 gm. calcium phosphate I found—

	By my method.		By Lasne's method.	
	$\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$. Grm.	Al_2O_3 . Grm.	$\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$. Grm.	Al_2O_3 . Grm.
1	0.0542	0.0220	0.0540	0.0226
2	0.0538	0.0225	0.0533	0.0223

In the analysis of a phosphate rock I found—

	By my method. Al_2O_3 found. Per cent.	By Lasne's method. Al_2O_3 found. Per cent.
	1.75 1.80	1.73 —

The detailed method used in my work is as follows:—Treat the finely-ground rock with a magnet to remove any metallic iron derived from the iron mortar used in the preparation of the sample. Dissolve 4 grms. of the rock in 30 c.c. dilute hydrochloric acid (1—1), heating just below the boiling-point for half an hour. This prevents the solution of pyrites. Filter into a 200 c.c. flask, add a few drops of nitric acid, and boil to oxidise the iron, cool, and dilute to mark. Take 50 c.c. containing 1 gm. of rock and run into 20 c.c. of the solution of C.P. caustic potash. Digest for an hour at 70°C ., stirring occasionally. Let the precipitate settle, and filter on a large paper, first decanting the supernatant liquid on the paper and finally washing on the precipitate. Wash two or three times with hot water.

To the filtrate add one gm. of ammonium phosphate, acidify with hydrochloric acid, add ammonia until a permanent precipitate is formed and dilute hydrochloric acid, drop by drop, until it is just dissolved. Add a mixture of 15 c.c. neutral ammonium acetate solution and 5 c.c. acetic acid (30 per cent) and digest for half an hour at 70°C ., by which time the precipitation is complete.

Filter, washing five or six times with hot ammonium acetate solution (10 per cent), stirring up the precipitate with the jet each time. Ignite with a low flame until the paper is charred, increase the heat, and, when the paper is completely consumed, blast for a minute. The precipitate is the normal aluminum phosphate, and its weight multiplied by the factor 0.418 gives the Al_2O_3 .

The iron oxide is determined volumetrically, preferably by the bichromate method, in a solution of the precipitate of iron oxide and calcium phosphate thrown down by the caustic potash. It is also determined separately, by the same method, in a solution of 5 grms. of the rock in dilute hydrochloric acid (1—1).

My thanks are due to Mr. H. E. Cutts, A.M., for valuable assistance in the above investigation.—*Journal of the American Chemical Society*, xviii., No. 8.

ON THE AMOUNT OF GOLD AND SILVER IN SEA-WATER.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

In the following paper are given the results of some experiments made with the object of determining the amount of gold in the sea-water off the coast of New South Wales.

* Read before the Royal Society of N. S. Wales.

The only reference that I can find in Sydney libraries relating to the presence of gold in sea-water are those of Sonstadt (CHEMICAL NEWS, xxvi., pp. 159, 160), which will be made use of later on in this paper, and a reference by Dr. T. Sterry Hunt ("Chemical and Geological Essays," London, 1879) to a Paper read before the American Association for the Advancement of Science, in 1866, by Professor Wurtz, in which he expressed an opinion that gold would be found in sea-water; but I cannot trace Prof. Wurtz's paper.

Then in 1894, Mr. E. C. C. Stanford, President of the Society of Chemical Industry, in his Address to the Members (Journ. Soc. Chem. Ind., xiii., July 31, 1894, p. 697), stated:—"The presence of gold has not been satisfactorily proved; it was expected it might accumulate in the copper sheathing of ships, and Messrs. Muntz obliged me with specimens of old sheathing, both copper and Muntz metal. Mr. Inglis, who kindly examined these for me, found both gold and silver, but not in larger proportion than usual."

The results were, per ton:—

	Copper Sheathing.			Muntz Metal.		
	Ozs.	dwt.	grs.	Ozs.	dwt.	grs.
Gold ..	0	2	21	0	1	15
Silver ..	4	12	9	5	3	12

Professor Judd, F.R.S., informed me that a Paper upon this subject was published in a Norwegian journal by Münster, about 1891, but I can find no reference to it in our Sydney libraries.

Sonstadt, in his Paper on the "Presence of Gold in Sea-water," gives various methods for the detection of the gold, and in a later letter to the CHEMICAL NEWS (vol. lxx., p. 131) refers to his previous communication of 1872, and states that the amount of gold is "far less than 1 grain per ton."

His first process is as follows:—Two or three decigrams of pure ferrous sulphate are dissolved in the water, which is acidulated by 2 or 3 drops of hydrochloric acid. The solution is heated in a chemically clean well-glazed porcelain dish, over a small flame, so managed that the flame may touch the under part of the dish without causing ebullition. Under these circumstances a lustrous film of iron oxide forms in the dish, commencing from the portion directly heated by the flame. The heat is continued, without boiling, until the sea-water is evaporated to about half, or so long as the film increases in extent and in lustre. The liquid is then poured off, the strongly adherent film is rinsed with a little water; and then about 50 c.c. of strong chlorine water is allowed to stand in the dish for an hour or two, after which it is slowly evaporated down (over the film) to a few drops, a drop of dilute hydrochloric acid being added towards the end of the evaporation. The liquid, which should be nearly colourless, is then poured into a test-glass containing a few drops of solution of stannous chloride, when, after a few minutes, the liquid takes a bluish or purplish tint, which may be exactly matched by a drop or two of a suitably diluted solution of gold added to a corresponding portion of tinsalt in another glass."

The sea-water first examined was collected from the coast at Coogee, away from any fresh water or other drainage. Eleven trials of this water were made with 200 c.c., as recommended by Sonstadt, but no trace of a purple or even pink tint was obtained, but with 600 c.c. a faint amethyst tint was obtained after standing some time. As a rule, after adding the stannous chloride, a white or grey precipitate came down in the course of a few days, and this precipitate in many cases became pink, purple, or slate-coloured.

To check Sonstadt's method various experiments were carried out. Gold chloride (from pure metal dissolved in chlorine water) was added to Coogee sea-water in the proportion of 1 grain of gold to the ton, and 200 c.c. of this was treated by Sonstadt's process on March 19th,

1895, when a light brown precipitate was thrown down by the stannous chloride; on the 27th the precipitate was of a red colour below with a pale pink layer above; on the 3rd of April the pink tint was more decided. Hence, if allowed to stand for a few days, the test will detect in 200 c.c. the presence of added gold in the proportion of 1 grain to the ton of sea-water, the gold originally present only being recognisable in 600 c.c.

On December 11th, 1894, a litre of the Coogee sea-water was concentrated and the test applied; no trace of pink or purple appeared, but on February 8th, 1895, a slight brown sediment had formed, which may have been due to gold.

Next, 2 litres were treated on December 28th, 1894, and allowed to stand until February 8th, 1895, when a faint pink tint was observable on the surface of the white precipitate. The second chlorine water extract of the film yielded a white precipitate which also had acquired a pink tint on February 8th.

On August 14th, 1895, two more samples, each of 2 litres of Coogee water, were tested. On the 15th the precipitates were brownish; the brownish tint seems to be due to the presence of gold. The contents of the two test-tubes were mixed together, dried, and scorified with 250 grains of assay lead free from gold, when a small bead of gold was obtained.

Sonstadt's second method was also tried, i.e., with barium chloride, as follows:—"From half a litre to a litre of sea-water should be taken for the experiment. As much solution of pure chloride of barium is added to the water as will give a grain of precipitate. A day or two should be allowed for the precipitate to settle. The precipitate is collected, dried, mixed with borax and lead, and the button of lead obtained before the blowpipe on charcoal is cupelled. The bead obtained is yellowish white, of the same colour as an alloy of sixty parts of gold to forty parts of silver, or thereabout. For confirmation of the presence of gold the bead may be dissolved in a very small test-tube, in a few drops of aqua regia, which is then evaporated, at a gentle heat, nearly to dryness. A few drops of pure hydrochloric acid are added, and the solution again evaporated, to destroy the excess of nitric acid. The solution is evaporated very nearly, but not quite, to dryness, a few drops of water are added, and the mixture warmed, and, when the chloride of silver is settled, a drop of solution of stannous chloride is allowed to fall down the side of the tube into the liquid, when the characteristic gold reaction is obtained."

Sonstadt's barium chloride method was tried on sea-water from off Jervis Bay as well as from the coast of Coogee, but the yield of gold was either much less than by the ferrous sulphate method (see further on) or no gold at all was obtained, even when two or more litres were used. Similar results were obtained from the use of stannous chloride and mercuric chloride together. Mercuric chloride alone and afterwards precipitated by hydrogen sulphide gave fairly good results. It was thought that the previous addition of sulphurous acid, oxalic acid, and other reducing substances, might increase the amount of gold obtained, but this was not found to be the case,—on the contrary, the yield was reduced.

As the result of a very large number of experiments with the film test upon gold chloride in distilled water and in sea-water, it was found that—

1. All the gold is not carried down by the film—not even by repeating the process and obtaining a second film; a little gold still being obtainable by a third film.
2. Neither is all the gold extracted by one treatment of the film with chlorine water.
3. Some of the gold is left on the dish in evaporating the chlorine water solution.
4. Several days and even weeks were required, in many cases, for the colour reaction to appear.

Gold in Sea-water along the Coast of New South Wales.

Next, a set of experiments was made upon water collected out at sea: twelve samples, two Winchester quarts of each, were kindly collected for me by Captain Hutton, of the N. S. Wales Government steamer *Thetis*, by direction of Mr. C. W. Darley, then Engineer-in-Chief for Harbours and Rivers, to whom my thanks are due for the ready assistance he has given me in this and other similar matters. Prior to being sent out the bottles were carefully cleaned, numbered, and packed in cases (each holding two bottles) so as to ensure purity and prevent error, and each bottle was rinsed with sea-water when about to be filled.

(To be continued).

NOTICES OF BOOKS.

"*Made in Germany.*" By ERNEST EDWIN WILLIAMS.
London: William Heinemann.

The most appropriate motto for this work would be—

" 'T is true, and pity 't is 't is true."

Mr. Williams enters upon his needful but thankless task with a survey of the "Departing Glory." What is the "glory" which is departing, and whose it was, needs little demonstration, and can scarcely be refuted by calling the author a Cassandra, whose prophecies of evil turned out to be true in the end.

The decline of our national industries is next discussed, under the heads of "Iron and Steel," "Ships, Hardware, and Machines," "Textiles," "Chemicals," and the "Lesser Trades." Then come the decisive questions, why Germany beats us? what must we do to be saved? The answers to these questions are manifold: lower wages and longer hours of labour are considered first, and are admitted to be causes, though not the one and greatest cause, of British decline and of alien success. The author contends that "the shortening of the hours of labour not unfrequently results in increased productivity." This is quite true up to a certain limit. A man may do more work in ten than in twelve hours, but can he do more in eight than in ten hours?

Strikes he recognises as one of the causes of our success; but he fails to discriminate between the classes of strikes. If by their means the supply of some indispensable article is suspended,—e.g., the output of coal,—the mischief is incalculable, and falls upon a variety of arts.

The denunciation of German goods as "billig und schlecht"—or as it here misprinted "blessig und schnell"—is fast losing its truthfulness.

The "Merchandise Marks Act" of 1897 is quoted as one of the causes of successful German competition. The author thinks rightly, that either "the Act is not wanted at all, or it does not go far enough," but he notices that "anyhow it makes for honesty." And in the alien success which he deplores honesty is greatly lacking. We know that a middleman, a traveller, calling upon a consumer in another foreign country, has been known to offer as British goods not manufactured in Britain at all, and of a decidedly inferior quality. When these are complained of, the vendor, with seeming candour, admits that British products have of late fallen off in quality, and suggests that German products will give more satisfaction. If an order is obtained, a list of German goods is sent in purposely of a better quality than those ordinarily "made in Germany," and so the thin end of the wedge is inserted.

Another stratagem is often tried where a British firm is induced, by boasted "intellectual interest," to employ alien clerks and book-keepers. Passing a ploughed field in the West Riding, our eyes fell upon a sheet of MS. It contained a list of the names and addresses of important

firms in South America, annotated with the peculiar predilections of each, in the style of packing up goods. The language and the characters were German, and the document was obviously intended to have been sent to some German agent or middleman.

Conveyance of goods is one of the factors in undermining the British manufacturer. For a ton of the same class of goods he has often to pay more per mile on an English railway than do alien goods of the same kind, for the same distance, on the same line. Thus a bounty is given to the enemy! Even some of our own colonies grant differential rates in favour of the alien.

Education is a remaining factor. We professed, some score of years ago, to be struck with the ignorance of our own people, and, at the cost of millions untold, we have been striving to force elementary literary education upon that part of our population which least needs it. Our manufacturers, our managers, overlookers, and the like, are the class who most need a higher training. The rank and file of the industrial army with us are quite as well educated as their continental opponents. What we want cannot be obtained from Board Schools.

We most strongly advise all intelligent and patriotic Englishmen to study this book carefully, and lay its lessons to heart.

Catalogue of Chemical Apparatus, &c., and Chemicals
Manufactured and Sold by PHILIP HARRIS and Co., Ltd.,
Edmund St., Birmingham.

If we may judge from the number of firms who issue price lists of apparatus and chemicals, we must be moving in the right direction as far as chemical research and chemical industry are concerned. We fear, however, that on too many of the articles would appear the mark "made in Germany."

The Catalogue is rich in balances. In addition to the well-known instruments of Oertling we find, figured and described, those of Bunge, Becker, Kuhlmann, and Satorius.

No sets of decimal weights seem to be procurable in which the subdivisions of the gramme are made of bent wires, and in sets of 6, 3, 2, and 1, which is much more convenient than 5, 5, 2, 2, 1, as it involves the handling of fewer pieces.

Among burettes the instrument of Binks still maintains a place.

Gas analysis is evidently becoming more appreciated, and hence there is a growing variety of apparatus for its performance, such as Bunte's, Hempel's, Elliott's, the Orsat-Lunge, Orsat-Pryce, and Orsat-Müncke, which last is apparently made only by Philip Harris and Co.

Several forms of microscopes are here mentioned, and, what is a novel and very satisfactory feature, spectroscopes also are not ignored, as we too often see.

Lovibond's tintometer is very fully described, but singularly not under the head of colorimeters.

Jena glass figures prominently, and seems now under most circumstances superior to the time-honoured product of Bohemia.

The selection of reagents and other chemicals is very full, and will be found very useful to persons engaged in research. A few points, however, are rather perplexing. Thus we find among the aniline colours "fuschine" priced per ounce 2s., as against "magenta" (best) rod., and rosaniline acetate rs. 6d. These substances, as the names are commonly applied, ought to be identical. Whence, then, the difference in price? Eosine among the aniline colours is marked rs. 2d. per ounce, and in another part of the Catalogue rs. 6d.

Among rarities we note tellurium 28s. per grain, rubidium (metallic) 4s. 6d. per grain, cerium rs. 6d. per grain.

There is a very full supplemental list of the gas devices of Fletcher (now Fletcher, Russell, and Co., Ltd.). Such

of these appliances as we have had occasion to use have proved very satisfactory.

The Speed of Propagation of the Rays of Gravitation, and the Laws of their Action. ("Die Fortpflanzungs-Geschwindigkeit der Schwerkraftstrahlen und deren Wirkungsgesetze"). By RUDOLF MEWES, Engineer and Physicist. Berlin: M. Kroyn, (Fischer's "Technologischer Verlag"). 1896. Pp. 96.

THE author is to a certain extent developing the ideas laid down by Christian Huyghens. From considerations which the mathematician alone can duly appreciate, he comes to the conclusion that the molar attraction is merely an especial form of the ethereal oscillations of heat, and that this physical force is the prime cause of all other forms of energy, the latter, according to the nature of the existing medium, appearing to us as light, electricity, and in general molecular attraction and general attraction of masses.

Hongkong. Report of the Government Analyst. June 20, 1896.

THE Government Analyst, W. E. Crow, states that 245 articles have been examined in the Government Laboratory. These included 11 toxicological cases, 53 potable waters, 168 petroleum, 4 milk, 23 cases under the morphine ordinance, 17 alcoholic liquors, and 29 miscellaneous articles. The toxicological cases included three attempts of human poisoning, one of which proved fatal. The drug used was the root of Tün Cheang ts' ó (*Gelsemium elegans*).

Orpiment (arsenic tersulphide) was used in an attempt to poison six men of No. 3 Section, A Company, Hongkong Regiment. The specimen examined contained 33.74 grains of arsenic tersulphide, a substance easily procurable in the Far East. All the patients recovered. In the remaining case—apparently not fatal—the drug used was probably the active principle of *Datura alba* (Nau yung, &c.). The offender was convicted.

The samples of water from the Frokfolloom, Tailum, and Kowloom supplies were all found excellent, but many of the town wells were highly polluted. The wells are, in many cases, merely holes in the ground, a few feet deep, lined with loose granite block.

The samples of milk are pronounced excellent, "even as compared with the best dairy samples obtained in Britain."

Of the alcoholic liquors, one is "said to have been prepared from the penes of three animals and harts-horn" (!).

The laboratory has been refitted, and is supplied with two balances by Becker and one of the Roberval type.

General Scientific Congress of Chile of 1894. ("Congreso Científico General Chileno"). Santiago de Chile: Cervantes. 1895.

THIS publication gives an account of a late meeting of a body which has a strong resemblance to the British Association. Its sections number nine, to wit:—1. Mathematics, Pure and Applied. 2. Physical and Chemical Sciences. 3. Medicine and Pharmacy. 4. Biology. 5. Geology and Mineralogy. 6. Geography, Physical and Astronomical. 7. History, Philology, and Ethnology. 8. Psychology and Pedagogics. And lastly, 9, Sociology, Law, and Political Economy.

To us the last three sections seem very much out of place, though on this subject we must speak mildly so long as our British Association retains its deplorable section for Statistics and Economy. We must note that the Chilean Association, in its 8th rule, stipulates that political or religious questions "may not be discussed in any section." To obey this rule we suggest that Sect. 9 should be eliminated.

The sections are classified under three groups. In the first of these figure, along with mathematics, physics, chemistry, geology and mineralogy, physical geography and astronomy. In the second, biology is worked along with pharmacy and medicine.

Among the principal papers read are "Chemical Investigations on *Margarodes vitium*," by Dr. Narciso Briones; "Influence of Chlorine on Ores of Gold and Silver," by Fernando Gautin; "Observations on the Normal Composition of the Well-waters of Santiago," by Pablo Letemeyer; and "Accidents caused by Venomous Insects in Chile," by Dr. Francisco C. Guzman.

"Spelling reform" seems to be attacking the Chileans in an aggravated form.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxliii., No. 8, August 24, 1896.

Electric Convection following the Lines of Force produced by Röntgen's Rays.—Auguste Righi.—In my various publications on the electric phenomena produced by the X rays I have always interpreted the facts observed as if it was demonstrated that the mechanism of the propagation of electricity is the same as on the dispersion by sharp points, or the dispersion on the surface of conductors heated to redness, or the dispersion produced by the ultra-violet rays. I reserve it to myself to show, in a memoir comprising the whole of my researches on these phenomena, in whatever manner the electricity is propagated in gases traversed by these rays. I think it well to make known at present some experiments which appear to me conclusive. It seems to me that the experiments clearly show the existence of a connection following the lines of force, and thus confirm my old views on the mechanism of the propagation of electricity in gases. I am happy to notice the agreement between my view and that which has been recently formulated by M. Villari. This physicist infers from his ingenious experiments that the dispersion produced by the X rays is a convection.

Utility in Radiography of Screens of Phosphorescent Zinc Sulphide; the Emission by Glowworms of Rays Traversing the Needle Paper.—Charles Henry.—I substitute for the simple fluorescent screens of barium platino-cyanide, calcium tungstate, &c., a screen of my phosphorescent zinc sulphide, covered with a leaf of "needle paper," and I lay on the paper the object to be radiographed. After some minutes' exposure to the radiation of the Crookes tube I remove the screen into the dark chamber; the depressions of the objects, opaque to the X rays, appear black and the transparent parts appear light. I can study the minutest details of the image for a quarter of an hour at least. On gently heating the screen with a source of dark heat I can continue this examination longer. This method, which allows of a great economy of electric energy and of tubes may be recommended for exhibitions, lectures, and all cases where it is not required to preserve the radiographic specimen. Phosphorescent zinc sulphide is incomparably more sensitive to the X rays than is calcium sulphide. If we expose for five minutes to one and the same radiation from the tube a plate enamelled with calcium sulphide and a screen of zinc sulphide, the former scarcely shines, whilst the latter is near its luminous saturation. During the last evenings I have had occasion to place during times varying from half an hour to several hours, some glowworms upon photographic plates wrapped up in needle-paper: on developing we could distinguish on the plate black and

white tracks which reproduced exactly the course pursued by the subventral lanterns of these capricious animals.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. i., No. 7.

Review of a Treatise by L. Holborn and Willy Wien on the Determination of High Temperatures.—R. Maesse.—This treatise cannot be reproduced without the eleven accompanying figures. The author's conclusions are as follows:—1. The measures of temperatures by means of observations of resistances are less exact than those effected with the thermo-electric couple, platinum-rhodium-platinum. If we check the resistance in the cold after each measurement, we often observe important variations. As the coefficient of temperature also varies this reaction can offer little guarantee. 2. Callendar's formula does not explain the facts with such accuracy that we could found upon it extended extrapolations. 3. The thermo-electric couple may be easily compared with the air thermometer, since it may be without difficulty introduced into the recipient of the latter. Even if the temperature is not very uniformly distributed in the furnace, the couple takes exactly the temperature of the mass of air of the thermometer.

MISCELLANEOUS.

The South-West London Polytechnic Institute, Chelsea.—This institute was only opened last October, and already some 1400 students have availed themselves of its educational advantages. The work hitherto has been mainly in the evening, but on September 29th the Institute will be opened to Day Students in Mathematics, Mechanics, Mechanism, Architecture, and Building Construction, Drawing Office Work, Workshops, Electrical Technology, Physics, Physical and Electrical Laboratories, Chemistry, Chemical Laboratory, and Applied Art. The hours will be from 10 a.m. to 1 p.m., and from 2 to 5 p.m. on each working day, except Saturday, when the hours will be from 10 a.m. to 1 p.m. The student may, for a very moderate fee, go through a complete course of Electrical Engineering, Mechanical Engineering, Architecture, Technical Chemistry, Applied Art, and Colonial Training, in two years, provided he can devote his whole daytime to the work. If he cannot devote his whole time in the day to the work, the classes are so arranged that he may, nevertheless, go through a precisely similar course in three, four, or more years; and as similar courses are provided in the evening, the opportunity is afforded him of shortening the period by attending evening as well as day classes. The education will be given partly by lectures and exercise classes, but mainly through the laboratory and workshop practice of the students themselves.

Programme of the Royal Technical High School at Aachen.—For the year 1896-97, October 1st to July 31st.—The curricula in this institution are not merely exceedingly complete, but are capable of being modified according to the destination of each student. There are courses for Architects, Constructive Engineers, Surveyors, Mechanical Engineers (with a view to Electro-technics), Mining Engineers (for the service of the State and for private undertakings), Metallurgists, Chemists, and Electro-chemists. Each course is arranged for four years. The curriculum for Chemists includes:—Construction of buildings, technology, organic experimental chemistry, inorganic experimental chemistry, chemistry of metals, national economy, higher mathematics, mechanics, and experimental physics. In the second year follow:—Technology, encyclopædic doctrine of machines, building machines, crystallography and mineralogy, exercises in

determining minerals, chemistry of benzene and pyridine, volumetric analysis, study of salt springs, technical chemistry, and for food chemists; botany (general, special, and microscopic). In the third year follow:—Introduction into the metallurgy of iron and of other metals, general geology, doctrine of strata, installation of chemical works, practice in microscopic botany (for food chemists), practical telegraphy and telephony. In the fourth year follows the theory of electro-chemistry. In a parallel column is mentioned industrial hygiene and a number of subjects which appear to us simply a waste of time and of brain-power, e.g., history of national economy, select chapters on statistics, the German law on bills of exchange, German insurance of workmen, doctrine of finance, and encyclopædia of law. Under the conditions which prevail in Britain, we should pronounce the study of finance, statistics, the law of bills of exchange, and financial doctrines, an utter waste of time for the chemist. The only legal matters with which he may advantageously concern himself are patent law and perhaps toxicology. We think that the questions of the water supply of towns and the treatment of waste waters, domestic and industrial, belong to the chemist, and not to the engineer. We do not see that in the studies required for the chemist sufficient weight is laid on the use of the microscope and the spectroscope.

Questionable Application of Science.—In a technical contemporary we find the following passage, which, whether its assertions are true or false, claims the attention of analysts:—"Scientific training seems very often to be diverted into curious channels. A large calico-printer recently informed us that the chemical knowledge of the German drug and dyestuff manufacturers seemed to be devoted entirely to the art of defeating tests rather than to the manufacture of drugs to pass genuine muster. It was the Germans who introduced that dangerous adulterant in Portland cement—gypsum, to wit,—entirely with a view to circumventing the American tests for cement. It matters not to the Germans that their cement is rendered dangerous, and that better results can be attained by safe means at very trifling cost. They have found an adulterant to serve a merely temporary purpose, and that is all they care to do. The Japanese seem to be following on similar lines. It would be amusing were it not so pitiable."

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LIVERPOOL, 1896.

INAUGURAL ADDRESS OF THE PRESIDENT,
SIR JOSEPH LISTER, BART., D.C.L., LL.D., F.R.S.

(Concluded from p. 143).

I ASK your indulgence if I have seemed to dwell too long upon matters in which I have been personally concerned. I now gladly return to the labours of others.

The striking results of the application of the germ theory to Surgery acted as a powerful stimulus to the investigation of the nature of the micro-organisms concerned; and it soon appeared that putrefaction was by no means the only evil of microbic origin to which wounds were liable. I had myself very early noticed that hospital gangrene was not necessarily attended by any unpleasant odour; and I afterwards made a similar observation regarding the matter formed in a remarkable epidemic of erysipelas in Edinburgh obviously of infective character. I had also seen a careless dressing followed by the occurrence of suppuration without putrefaction. And as these non-putrefactive disorders had the same self-propagating property as ferments, and were suppressed by the same antiseptic agencies which were used for combating the putrefactive microbes, I did not doubt that they were of an analogous origin; and I ventured to express the view that, just as the various fermentations had each its special microbe, so it might be with the various complications of wounds. This surmise was afterwards amply verified. Professor Ogston, of Aberdeen, was an early worker in this field, and showed that in acute abscesses, that is to say those which run a rapid course, the matter, although often quite free from unpleasant odour, invariably contains micro-organisms belonging to the group which, from the spherical form of their elements, are termed micrococci; and these he classed as streptococci or staphylococci, according as they were arranged in chains or disposed in irregular clusters like bunches of grapes. The German pathologist, Fehleisen, followed with a beautiful research, by which he clearly proved that erysipelas is caused by a streptococcus. A host of earnest workers in different countries have cultivated the new science of Bacteriology, and, while opening up a wide fresh domain of Biology, have demonstrated in so many cases the casual relation between special micro-organisms and special diseases, not only in wounds but in the system generally, as to afford ample confirmation of the induction which had been made by Pasteur that all infective disorders are of microbic origin.

Not that we can look forward with anything like confidence to being able ever to see the *materies morbi* of every disease of this nature. One of the latest of such discoveries has been that by Pfeiffer, of Berlin, of the bacillus of influenza, perhaps the most minute of all micro-organisms ever yet detected. The bacillus of anthrax, the cause of a plague common among cattle in some parts of Europe, and often communicated to sorters of foreign wool in this country, is a giant as compared with this tiny being; and supposing the microbe of any infectious fever to be as much smaller than the influenza bacillus as this is less than that of anthrax, a by no means unlikely hypothesis, it is probable that it would never be visible to man. The improvements of the microscope,

based on the principle established by my father in the earlier part of the century, have apparently nearly reached the limits of what is possible. But that such parasites are really the causes of all this great class of diseases can no longer be doubted.

The first rational step towards the prevention or cure of disease is to know its cause; and it is impossible to over-estimate the practical value of researches such as those to which I am now referring. Among their many achievements is what may be fairly regarded as the most important discovery ever made in pathology, because it revealed the true nature of the disease which causes more sickness and death in the human race than any other. It was made by Robert Koch, who greatly distinguished himself, when a practitioner in an obscure town in Germany, by the remarkable combination of experimental acuteness and skill, chemical and optical knowledge, and successful micro-photography, which he brought to bear upon the illustration of infective diseases of wounds in the lower animals, in recognition of which service the enlightened Prussian Government at once appointed him to an official position of great importance in Berlin. There he conducted various important researches; and at the London Congress in 1881 he showed to us for the first time the bacillus of tubercle. Wonderful light was thrown by this discovery upon a great group of diseases which had before been rather guessed than known to be of an allied nature; a precision and efficacy never before possible was introduced into their surgical treatment, while the physician became guided by new and sure light as regards their diagnosis and prevention.

At that same London Congress Koch demonstrated to us his "plate culture" of bacteria, which was so important that I must devote a few words to its description. With a view to the successful study of the habits and effects of any particular microbe outside the living body, it is essential that it should be present unmixed in the medium in which it is cultivated. It can be readily understood how difficult it must have been to isolate any particular micro-organism when it existed mixed, as was often the case, with a multitude of other forms. In fact, the various ingenious attempts made to effect this object had often proved entire failures. Koch, however, by an ingenious procedure converted what had been before impossible into a matter of the utmost facility. In the broth or other nutrient liquid which was to serve as food for the growing microbe, he dissolved, by aid of heat, just enough gelatin to ensure that, while it should become a solid mass when cold, it should remain fluid though reduced in temperature so much as to be incapable of killing living germs. To the medium thus partially cooled was added some liquid containing, among others, the microbe to be investigated; and the mixture was thoroughly shaken so as to diffuse the bacteria and separate them from each other. Some of the liquid was then poured out in a thin layer upon a glass plate and allowed to cool so as to assume the solid form. The various microbes, fixed in the gelatin and so prevented from intermingling, proceeded to develop each its special progeny, which in course of time showed itself as an opaque speck in the transparent film. Any one of such specks could now be removed and transferred to another vessel in which the microbe composing it grew in perfect isolation.

Pasteur was present at this demonstration, and expressed his sense of the great progress effected by the new method. It was soon introduced into his own Institute and other laboratories throughout the world, and it has immensely facilitated bacteriological study.

One fruit of it in Koch's own hands was the discovery of the microbe of cholera in India, whither he went to study the disease. This organism was termed by Koch, from its curved form, the "comma bacillus," and by the French the cholera vibrio. Great doubts were for a long time felt regarding this discovery. Several other kinds of bacteria were found of the same shape, some of them producing very similar appearances in culture media.

But bacteriologists are now universally agreed that, although various other conditions are necessary to the production of an attack of cholera besides the mere presence of the vibrio, yet it is the essential *materies morbi*; and it is by the aid of the diagnosis which its presence in any case of true cholera enables the bacteriologist to make, that threatened invasions of this awful disease have of late years been so successfully repelled from our shores. If bacteriology had done nothing more for us than this, it might well have earned our gratitude.

I have next to invite your attention to some earlier work of Pasteur. There is a disease known in France under the name of *choléra des poules*, which often produced great havoc among the poultry yards of Paris. It had been observed that the blood of birds that had died of this disease was peopled by a multitude of minute bacteria, not very dissimilar in form and size to the microbe of the lactic ferment to which I have before referred. And Pasteur found that, if this bacterium was cultivated outside the body for a protracted period under certain conditions, it underwent a remarkable diminution of its virulence; so that, if inoculated into a healthy fowl, it no longer caused the death of the bird, as it would have done in its original condition, but produced a milder form of the disease which was not fatal. And this altered character of the microbe, caused by certain conditions, was found to persist in successive generations cultivated in the ordinary way. Thus was discovered the great fact of what Pasteur termed the *atténuation des virus*, which at once gave the clue to understanding what had before been quite mysterious, the difference in virulence of the same disease in different epidemics.

But he made the further very important observation that a bird which had gone through the mild form of the complaint had acquired immunity against it in its most virulent condition. Pasteur afterwards succeeded in obtaining mitigated varieties of microbes for some other diseases, and he applied with great success the principle which he had discovered in fowl-cholera for protecting the larger domestic animals against the plague of anthrax. The preparations used for such preventive inoculations he termed "vaccins," in honour of our great countryman Edward Jenner. For Pasteur at once saw the analogy between the immunity to fowl-cholera produced by its attenuated virus and the protection afforded against smallpox by vaccination. And while pathologists still hesitated, he had no doubt of the correctness of Jenner's expression, *variola vaccina*, or smallpox in the cow.

It is just a hundred years since Jenner made the crucial experiment of inoculating with smallpox a boy whom he had previously vaccinated, the result being, as he anticipated, that the boy was quite unaffected. It may be remarked that this was a perfectly legitimate experiment, involving no danger to the subject of it. Inoculation was at that time the established practice; and if vaccination should prove nugatory, the inoculation would be only what would have been otherwise called for, while it would be perfectly harmless if the hoped-for effect of vaccination had been produced.

We are a practical people, not much addicted to personal commemorations; although our nation did indeed celebrate with fitting splendour the jubilee of the reign of our beloved Queen, and at the invitation of Glasgow the scientific world has lately marked in a manner, though different, as imposing, the jubilee of the life-work of a sovereign in science (Lord Kelvin). But while we cannot be astonished that the centenary of Jenner's immortal discovery should have failed to receive general recognition in this country, it is melancholy to think that this year should, in his native county, have been distinguished by a terrible illustration of the results which would sooner or later inevitably follow the general neglect of his prescriptions.

I have no desire to speak severely of the Gloucester Guardians. They are not sanitary authorities, and had not the technical knowledge necessary to enable them to

judge between the teachings of true science and the declamations of misguided, though well-meaning, enthusiasts. They did what they believed to be right; and when roused to a sense of the greatness of their mistake, they did their very best to repair it, so that their city is said to be now the best vaccinated in Her Majesty's dominions. But though by their praiseworthy exertions they succeeded in promptly checking the raging epidemic, they cannot recall the dead to life, or restore beauty to marred features, or sight to blinded eyes. Would that the entire country and our Legislature might take duly to heart this object-lesson!

How completely the medical profession were convinced of the efficacy of vaccination in the early part of this century was strikingly illustrated by an account given by Professor Crookshank, in his interesting history of this subject, of several eminent medical men in Edinburgh meeting to see the—to them—unprecedented fact of a vaccinated person having taken smallpox. It has, of course, since become well known that the milder form of the disease, as modified by passing through the cow, confers a less permanent protection than the original human disorder. This it was, of course, impossible for Jenner to foresee. It is, indeed, a question of degree, since a second attack of ordinary smallpox is occasionally known to occur, and vaccination, long after it has ceased to give perfect immunity, greatly modifies the character of the disorder and diminishes its danger. And, happily, in re-vaccination after a certain number of years we have the means of making Jenner's work complete. I understand that the majority of the Commissioners, who have recently issued their report upon this subject, while recognising the value and importance of re-vaccination, are so impressed with the difficulties that would attend making it compulsory by legislation that they do not recommend that course; although it is advocated by two of their number who are of peculiarly high authority on such a question. I was lately told by a Berlin professor that no serious difficulty is experienced in carrying out the compulsory law that prevails in Germany. The masters of the schools are directed to ascertain in the case of every child attaining the age of twelve whether re-vaccination has been practised. If not, and the parents refuse to have it done, they are fined one mark. If this does not prove effectual, the fine is doubled; and if even the double penalty should not prove efficacious, a second doubling of it would follow, but, as my informant remarked, it is very seldom that it is called for. The result is that smallpox is a matter of extreme rarity in that country; while it is absolutely unknown in the huge German army, in consequence of the rule that every soldier is re-vaccinated on entering the service. Whatever view our Legislature may take on this question, one thing seems to me clear,—that it will be the duty of Government to encourage by every available means the use of calf lymph, so as to exclude the possibility of the communication of any human disease to the child, and to institute such efficient inspection of vaccination institutes as shall ensure careful antiseptic arrangements, and so prevent contamination by extraneous microbes. If this were done, "conscientious objections" would cease to have any rational basis. At the same time, the administration of the regulations on vaccination should be transferred (as advised by the Commissioners) to competent sanitary authorities.

But to return to Pasteur. In 1880 he entered upon the study of that terrible but then most obscure disease, Hydrophobia or Rabies, which from its infective character he was sure must be of microbic origin, although no micro-organism could be detected in it. He early demonstrated the new pathological fact that the virus had its essential seat in the nervous system. This proved the key to his success in this subject. One result that flowed from it has been the cause of unspeakable consolation to many. The foolish practice is still too prevalent of killing the dog that has bitten any one, on the absurd notion, that if it were mad, its destruction would prevent

the occurrence of hydrophobia in the person bitten. The idea of the bare possibility of the animal having been so affected causes an agony of suspense during the long weeks or months of possible incubation of the disease. Very serious nervous symptoms aping true hydrophobia have been known to result from the terror thus inspired. Pasteur showed that if a little of the brain or spinal cord of a dog that had been really mad was inoculated in an appropriate manner into a rabbit, it infallibly caused rabies in that animal in a few days. If therefore such an experiment was made with a negative result, the conclusion might be drawn with certainty that the dog had been healthy. It is perhaps right that I should say that the inoculation is painlessly done under an anæsthetic, and that in the rabbit rabies does not assume the violent form that it does in the dog, but produces gradual loss of power with little if any suffering.

This is the more satisfactory because rabbits in which the disease has been thus artificially induced are employed in carrying out what was Pasteur's greatest triumph,—the preventive treatment of hydrophobia in the human subject. We have seen that Pasteur discovered that microbes might under some circumstances undergo mitigation of their virulence. He afterwards found that under different conditions they might have it exalted, or, as he expressed it, there might be a *renforcement du virus*. Such proved to be the case with rabies in the rabbit; so that the spinal cords of animals which had died of it contained the poison in a highly intensified condition. But he also found that if such a highly virulent cord was suspended under strict antiseptic precautions in a dry atmosphere at a certain temperature, it gradually from day to day lost in potency, till in course of time it became absolutely inert. If now an emulsion of such a harmless cord was introduced under the skin of an animal, as in the subcutaneous administration of morphia, it might be followed without harm another day by a similar dose of a cord still rather poisonous; and so from day to day stronger and stronger injections might be used, the system becoming gradually accustomed to the poison, till a degree of virulence had been reached far exceeding that of the bite of a mad dog. When this had been attained, the animal proved incapable of taking the disease in the ordinary way; and more than that, if such treatment was adopted after an animal had already received the poison, provided that too long a time had not elapsed, the outbreak of the disease was prevented. It was only after great searching of heart that Pasteur, after consultation with some trusted medical friends, ventured upon trying this practice upon man. It has since been extensively adopted in various parts of the world with increasing success as the details of the method were improved. It is not of course the case that every one bitten by a really rabid animal takes the disease; but the percentage of those who do so, which was formerly large, has been reduced almost to zero by this treatment, if not too long delayed.

While the intensity of rabies in the rabbit is undoubtedly due to a peculiarly virulent form of the microbe concerned, we cannot suppose that the daily diminishing potency of the cord suspended in dry warm air is an instance of attenuation of virus, using the term "virus" as synonymous with the microbe concerned. In other words, we have no reason to believe that the special micro-organism of hydrophobia continues to develop in the dead cord and produce successively a milder and milder progeny, since rabies cannot be cultivated in the nervous system of a dead animal. We must rather conclude that there must be some chemical poison present which gradually loses its potency as time passes. And this leads me to refer to another most important branch of this large subject of bacteriology,—that of the poisonous products of microbes.

It was shown several years ago, by Roux and Yersin, working in the *Institut Pasteur*, that the crust or false membrane which forms upon the throats of patients affected with diphtheria contains bacteria which can be

cultivated outside the body in a nutrient liquid, with the result that it acquires poisonous qualities of astonishing intensity, comparable to that of the secretion of the poison-glands of the most venomous serpents. And they also ascertained that the liquid retained this property after the microbes had been removed from it by filtration, which proved that the poison must be a chemical substance in solution, as distinguished from the living element which had produced it. These poisonous products of bacteria, or toxins as they have been termed, explain the deadly effects of some microbes, which it would otherwise be impossible to understand. Thus, in diphtheria itself the special bacillus which was shown by Löffler to be its cause, does not become propagated in the blood, like the microbe of chicken cholera, but remains confined to the surface on which it first appeared; but the toxin which it secretes is absorbed from that surface into the blood, and so poisons the system. Similar observations have been made with regard to the microbes of some other diseases, as, for example, the bacillus of tetanus or lockjaw. This remains localised in the wound, but forms a special toxin of extreme potency, which becomes absorbed and diffused through the body.

Wonderful as it seems, each poisonous microbe appears to form its own peculiar toxin. Koch's tuberculin was of this nature, a product of the growth of the tubercle bacillus in culture media. Here, again, great effects were produced by extremely minute quantities of the substance, but here a new peculiarity showed itself, viz., that patients affected with tubercular disease, in any of its varied forms, exhibited inflammation in the affected part and general fever after receiving under the skin an amount of the material which had no effect whatever upon healthy persons, I witnessed in Berlin some instances of these effects, which were simply astounding. Patients affected with a peculiar form of obstinate ulcer of the face showed, after a single injection of the tuberculin, violent inflammatory redness and swelling of the sore and surrounding skin; and, what was equally surprising, when this disturbance subsided the disease was found to have undergone great improvement. By repetitions of such procedures, ulcers which had previously been steadily advancing, in spite of ordinary treatment, became greatly reduced in size, and in some instances apparently cured. Such results led Koch to believe that he had obtained an effectual means of dealing with tubercular disease in all its forms. Unhappily, the apparent cure proved to be only of transient duration, and the high hopes which had been inspired by Koch's great reputation were dashed. It is but fair to say that he was strongly urged to publish before he was himself disposed to do so, and we cannot but regret that he yielded to the pressure put upon him.

But though Koch's sanguine anticipations were not realised, it would be a great mistake to suppose that his labours with tuberculin have been fruitless. Cattle are liable to tubercle, and, when affected with it, may become a very serious source of infection for human beings, more especially when the disease affects the udders of cows, and so contaminates the milk. By virtue of the close affinity that prevails between the lower animals and ourselves, in disease as well as in health, tuberculin produces fever in tubercular cows in doses which do not affect healthy beasts. Thus, by the subcutaneous use of a little of the fluid, tubercle latent in internal organs of an apparently healthy cow can be with certainty revealed, and the slaughter of the animal after this discovery protects man from infection.

It has been ascertained that glanders presents a precise analogy with tubercle as regards the effects of its toxic products. If the microbe which has been found to be the cause of this disease is cultivated in appropriate media, it produces a poison which has received the name of mallein, and the subcutaneous injection of a suitable dose of this fluid into a glandered horse causes striking febrile symptoms which do not occur in a healthy animal. Glanders, like tubercle, may exist in insidious latent

forms which there was formerly no means of detecting, but which are at once disclosed by this means. If a glandered horse has been accidentally introduced into a large stable, this method of diagnosis surely tells if it has infected others. All receive a little mallein. Those which become affected with fever are slaughtered, and thus not only is the disease prevented from spreading to other horses, but the grooms are protected from a mortal disorder.

This valuable resource sprang from Koch's work on tuberculin, which has also indirectly done good in other ways. His distinguished pupil, Behring, has expressly attributed to those researches the inspiration of the work which led him and his since famous collaborateur, the Japanese Kitasato, to their surprising discovery of anti-toxic serum. They found that if an animal of a species liable to diphtheria or tetanus received a quantity of the respective toxin so small as to be harmless, and afterwards, at suitable intervals, successively stronger and stronger doses, the creature, in course of time, acquired such a tolerance for the poison as to be able to receive with impunity a quantity very much greater than would at the outset have proved fatal. So far, we have nothing more than seems to correspond with the effects of the increasingly potent cords in Pasteur's treatment of rabies. But what was entirely new in their results was that, if blood was drawn from an animal which had acquired this high degree of artificial immunity, and some of the clear fluid or serum which exuded from it after it had clotted was introduced under the skin of another animal, this second animal acquired a strong, though more transient, immunity against the particular toxin concerned. The serum in some way counteracted the toxin, or was anti-toxic. But, more than that, if some of the anti-toxic serum was applied to an animal after it had already received a poisonous dose of the toxin, it preserved the life of the creature, provided that too long a time had not elapsed after the poison was introduced. In other words, the antitoxin proved to be not only preventive but curative.

Similar results were afterwards obtained by Ehrlich, of Berlin, with some poisons not of bacterial origin, but derived from the vegetable kingdom; and quite recently the independent labours of Calmette of Lille and Fraser of Edinburgh have shown that antidotes of wonderful efficacy against the venom of serpents may be procured on the same principle. Calmette has obtained anti-toxin so powerful that a quantity of it only a 200,000th part of the weight of an animal will protect it perfectly against a dose of the secretion of the poison-glands of the most venomous serpents known to exist, which without such protection would have proved fatal in four hours. For curative purposes larger quantities of the remedy are required, but cases have been already published by Calmette in which death appears to have been averted in the human subject by this treatment.

Behring's darling object was to discover means of curing tetanus and diphtheria in man. In tetanus the conditions are not favourable; because the specific bacilli lurk in the depths of the wound, and only declare their presence by symptoms caused by their toxin having been already in a greater or less amount diffused through the system; and in every case of this disease there must be a fear that the antidote may be applied too late to be useful. But in diphtheria the bacilli very early manifest their presence by the false membrane which they cause upon the throat, so that the anti-toxin has a fair chance; and here we are justified in saying that Behring's object has been attained.

The problem, however, was by no means so simple as in the case of some mere chemical poison. However effectual the anti-toxin might be against the toxin, if it left the bacilli intact, not only would repeated injections be required to maintain the transient immunity to the poison perpetually secreted by the microbes, but the

bacilli might by their growth and extension cause obstruction of the respiratory passages.

Roux, however, whose name must always be mentioned with honour in relation to this subject, effectually disposed of this difficulty. He showed by experiments on animals that a diphtheritic false membrane, rapidly extending and accompanied by surrounding inflammation, was brought to a stand by the use of the anti-toxin, and soon dropped off, leaving a healthy surface. Whatever be the explanation, the fact was thus established that the anti-toxic serum, while it renders the toxin harmless, causes the microbe to languish and disappear.

No theoretical objection could now be urged against the treatment; and it has during the last two years been extensively tested in practice in various parts of the world, and it has gradually made its way more and more into the confidence of the profession. One important piece of evidence in its favour in this country is derived from the report of the six large hospitals under the management of the London Asylums Board. The medical officers of these hospitals at first naturally regarded the practice with scepticism; but as it appeared to be at least harmless, they gave it a trial, and during the year 1895 it was very generally employed upon the 2182 cases admitted, and they have all become convinced of its great value. In the nature of things, if the theory of the treatment is correct, the best results must be obtained when the patients are admitted at an early stage of the attack, before there has been time for much poisoning of the system; and accordingly we learn from the Report that, comparing 1895 with 1894, during which latter year the ordinary treatment had been used, the percentage of mortality, in all the six hospitals combined, among the patients admitted on the first day of the disease, which in 1894 was 22·5, was only 4·6 in 1895; while for those admitted on the second day the numbers are 27 for 1894 and 14·8 for 1895. Thus for cases admitted on the first day the mortality was only one-fifth of what it was in the previous year, and for those entering on the second it was halved. Unfortunately in the low parts of London which furnish most of these patients the parents too often delay sending in the children till much later; so that on the average no less than 67·5 per cent were admitted on the fourth day of the disease or later. Hence the aggregate statistics of all cases are not nearly so striking. Nevertheless, taking it altogether, the mortality in 1895 was less than had ever before been experienced in those hospitals. I should add that there was no reason to think that the disease was of a milder type than usual in 1895, and no change whatever was made in the treatment except as regards the anti-toxic injections.

There is one piece of evidence recorded in the report which, though it is not concerned with high numbers, is well worthy of notice. It relates to a special institution to which convalescents from scarlet fever are sent from all the six hospitals. Such patients occasionally contract diphtheria, and when they do so the added disease has generally proved extremely fatal. In the five years preceding the introduction of the treatment with anti-toxin the mortality from this cause had never been less than 50 per cent, and averaged on the whole 61·9 per cent. During 1895, under anti-toxin, the deaths among the 119 patients of this class were only 7·5 per cent, or one-eighth of what had been previously experienced. This very striking result seems to be naturally explained by the fact that these patients being already in hospital when the diphtheria appeared, an unusually early opportunity was afforded for dealing with it.

There are certain cases of so malignant a character from the first that no treatment will probably ever be able to cope with them. But taking all cases together it seems probable that Behring's hope that the mortality may be reduced to 5 per cent will be fully realised when the public become alive to the paramount importance of having the treatment commenced at the outset of the disease.

There are many able workers in the field of Bacteriology whose names time does not permit me to mention, and to whose important labours I cannot refer; and even those researches of which I have spoken have been, of course, most inadequately dealt with. I feel this especially with regard to Pasteur, whose work shines out more brightly the more his writings are perused.

I have lastly to bring before you a subject which, though not bacteriological, has intimate relations with bacteria. If a drop of blood is drawn from the finger by a prick with a needle, and examined microscopically between two plates of glass, there are seen in it minute solid elements of two kinds, the one pale orange bi-concave discs, which, seen in mass, give the red colour to the vital fluid, the other more or less granular spherical masses of the soft material called protoplasm, destitute of colour, and therefore called the colourless or white corpuscles. It has been long known that if the microscope was placed at such a distance from a fire as to have the temperature of the human body, the white corpuscles might be seen to put out and retract little processes or pseudopodia, and by their means crawl over the surface of the glass, just like the extremely low forms of animal life termed—from this faculty of changing their form—*amœbæ*. It was a somewhat weird spectacle, that of seeing what had just before been constituents of our own blood moving about like independent creatures. Yet there was nothing in this inconsistent with what we knew of the fixed components of the animal frame. For example, the surface of a frog's tongue is covered with a layer of cells, each of which is provided with two or more lashing filaments or cilia, and those of all the cells acting in concert cause a constant flow of fluid in a definite direction over the organ. If we gently scrape the surface of the animal's tongue, we can detach some of these ciliated cells; and on examining them with the microscope in a drop of water we find that they will continue for an indefinite time their lashing movements, which are just as much living or vital in their character as the writhings of a worm. And, as I observed many years ago, these detached cells behave under the influence of a stimulus just like parts connected with the body, the movements of the cilia being excited to greater activity by gentle stimulation, and thrown into a state of temporary inactivity when the irritation was more severe. Thus each constituent element of our bodies may be regarded as in one sense an independent living being, though all work together in marvellous harmony for the good of the body politic. The independent movements of the white corpuscles outside the body were therefore not astonishing; but they long remained matters of mere curiosity. Much interest was called to them by the observations of the German pathologist Cohnheim, that in some inflammatory conditions they passed through the pores in the walls of the finest blood-vessels, and thus escaped into the interstices of the surrounding tissues. Cohnheim attributed their transit to the pressure of the blood. But why it was that, though larger than the red corpuscles, and containing a nucleus which the red ones have not, they alone passed through the pores of the vessels, or why it was that this emigration of the white corpuscles occurred abundantly in some inflammations and was absent in others, was quite unexplained.

These white corpuscles, however, have been invested with extraordinary new interest by the researches of the Russian naturalist and pathologist, Metchnikoff. He observed that, after passing through the walls of the vessels, they not only crawl about like *amœbæ*, but, like them, receive nutritious materials into their soft bodies and digest them. It is thus that the effete materials of a tadpole's tail are got rid of, so that they play a most important part in the function of absorption.

But still more interesting observations followed. He found that a microscopic crustacean, a kind of water-flea, was liable to be infested by a fungus which had exceedingly sharp-pointed spores. These were apt to penetrate

the coats of the creature's intestine, and project into its body-cavity. No sooner did this occur with any spore than it became surrounded with a group of the cells which are contained in the cavity of the body and correspond to the white corpuscles of our blood. These proceeded to attempt to devour the spore; and if they succeeded, in every such case the animal was saved from the invasion of the parasite. But if the spores were more than could be disposed of by the devouring cells (phagocytes, as Metchnikoff termed them), the water-flea succumbed.

Starting from this fundamental observation, he ascertained that the microbes of infective diseases are subject to this same process of devouring and digestion, carried on both by the white corpuscles and by cells that line the blood-vessels. And by a long series of most beautiful researches he has, as it appears to me, firmly established the great truth that phagocytosis is the main defensive means possessed by the living body against the invasions of its microscopic foes. The power of the system to produce anti-toxic substances to counteract the poisons of microbes is undoubtedly in its own place of great importance. But in the large class of cases in which animals are naturally refractory to particular infective diseases the blood is not found to yield any anti-toxic element by which the natural immunity can be accounted for. Here phagocytosis seems to be the sole defensive agency. And even in cases in which the serum does possess anti-toxic, or, as it would seem in some cases, germicidal properties, the bodies of the dead microbes must at last be got rid of by phagocytosis, and some recent observations would seem to indicate that the useful elements of the serum may be, in part at least, derived from the digestive juices of the phagocytes. If ever there was a romantic chapter in pathology, it has surely been that of the story of phagocytosis.

I was myself peculiarly interested by these observations of Metchnikoff's, because they seemed to me to afford clear explanation of the healing of wounds by first intention under circumstances before incomprehensible. This primary union was sometimes seen to take place in wounds treated with water-dressing; that is to say, a piece of wet lint covered with a layer of oiled silk to keep it moist. This, though cleanly, when applied, was invariably putrid within twenty-four hours. The layer of blood between the cut surfaces was thus exposed at the outlet of the wound to a most potent septic focus. How was it prevented from putrefying, as it would have done under such influence if, instead of being between divided living tissues, it had been between plates of glass or other indifferent material? Pasteur's observations pushed the question a step further. It now was, How were the bacteria of putrefaction kept from propagating in the decomposable film? Metchnikoff's phagocytosis supplied the answer. The blood between the lips of the wound became rapidly peopled with phagocytes, which kept guard against the putrefactive microbes and seized them as they endeavoured to enter.

If phagocytosis was ever able to cope with septic microbes in so concentrated and intense a form, it could hardly fail to deal effectually with them in the very mitigated condition in which they are present in the air. We are thus strongly confirmed in our conclusion that the atmospheric dust may be safely disregarded in our operations: and Metchnikoff's researches, while they have illumined the whole pathology of infective diseases, have beautifully completed the theory of antiseptic treatment in surgery.

I might have taken equally striking illustrations of my theme from other departments in which microbes play no part. In fact, any attempt to speak of all that the art of healing has borrowed from science and contributed to it during the past half-century would involve a very extensive dissertation on pathology and therapeutics. I have culled specimens from a wide field; and I only hope that in bringing them before you I have not overstepped the bounds of what is fitting before a mixed company. For

many of you my remarks can have had little if any novelty: for others they may perhaps possess some interest as showing that Medicine is no unworthy ally of the British Association—that, while her practice is ever more and more based on science, the ceaseless efforts of her votaries to improve what have been fittingly designated *Quæ prosunt omnibus artes*, are ever adding largely to the sum of abstract knowledge.

ADDRESS TO THE CHEMICAL SECTION
OF THE
BRITISH ASSOCIATION.
LIVERPOOL, 1896.

By Dr. LUDWIG MOND, F.R.S., President of the Section.

IN endeavouring to fix upon a suitable theme for the address I knew you would to-day expect from me, I have felt that I ought to give due consideration to the interests which tie this magnificent city of Liverpool, whose hospitality we enjoy this week, to Section B of the British Association.

I have therefore chosen to give you a brief history of the manufacture of chlorine, with the progress of which this city and its neighbourhood have been very conspicuously and very honourably connected, not only as regards quantity—I believe this neighbourhood produces to-day nearly as much chlorine as the rest of this world together—but more particularly by having originated, worked out, and carried into practice several of the most important improvements ever introduced into this manufacture. I was confirmed in my choice by the fact that this manufacture has been influenced and perfected in an extraordinary degree by the rapid assimilation and application of the results of purely scientific investigations and of new scientific theories, and offers a very remarkable example of the incalculable value to our commercial interests of the progress of pure science.

The early history of chlorine is particularly interesting, as it played a most important rôle in the development of chemical theories. There can be no doubt that the Arabian alchemist Geber, who lived eleven hundred years ago, must have known that "*Aqua Regia*," which he prepared by distilling a mixture of salt, nitre, and vitriol, gave off on heating very corrosive, evil-smelling, greenish yellow fumes, and all his followers throughout a thousand years must have been more or less molested by these fumes whenever they used *aqua regia*, the one solvent of the gold they attempted so persistently to produce.

But it was not until 1774 that the great Swedish chemist Scheele succeeding in establishing the character of these fumes. He discovered that on heating manganese with muriatic acid he obtained fumes very similar to those given off by "*aqua regia*," and found that these fumes constituted a permanent gas of yellowish green colour, very pungent odour, very corrosive, very irritating to the respiratory organs, and which had the power of destroying organic colouring-matters.

According to the views prevalent at the time, Scheele considered that the manganese had removed phlogiston from the muriatic acid, and he consequently called the gas dephlogisticated muriatic acid.

When during the next decade Lavoisier successfully attacked, and after a memorable struggle completely upset, the phlogiston theory and laid the foundations of our modern chemistry, Berthollet, the eminent "father" of physical chemistry—the science of to-day—endeavoured to determine the place of Scheele's gas in the new theory. Lavoisier was of opinion that all acids, including muriatic acid, contain oxygen. Berthollet found that a solution of Scheele's gas in water, when exposed to the sunlight, gives off oxygen and leaves behind muriatic acid. He considered this as proof that this gas consists of muriatic acid and oxygen, and called it oxygenated muriatic acid.

In the year 1785 Berthollet conceived the idea of utilising the colour destroying powers of this gas for bleaching purposes. He prepared the gas by heating a mixture of salt, manganese, and vitriol. He used a solution of the gas in water for bleaching, and subsequently discovered that the product obtained by absorbing the gas in a solution of caustic potash possessed great advantages in practice.

This solution was prepared as early as 1789, at the chemical works on the Quai de Javelle, in Paris, and is still made and used there under the name of "*Eau de Javelle*."

James Watt, whose great mind was not entirely taken up with that greatest of all inventions—his steam engine—by which he has benefitted the human race more than any other man, but who also did excellent work in chemistry—became acquainted in Paris with Berthollet's process, and brought it to Scotland. Here it was taken up with that energy characteristic of the Scotch, and a great stride forward was made when, in 1798, Charles Tennant, the founder of the great firm which has only recently lapsed into the United Alkali Company, began to use milk of lime in place of the more costly caustic potash, in making a bleaching liquid; and a still greater advance was made when, in the following year, Tennant proposed to absorb the chlorine by hydrate of lime, and thus to produce a dry substance, since known under the name of bleaching powder, which allowed the bleaching powers of chlorine to be transported to any distance.

In order to give you a conception of the theoretical ideas prevalent at this time, I will read to you a passage from an interesting treatise on the art of bleaching published in 1799 by Higgins. In his chapter "*On Bleaching with the Oxygenated Muriatic Acid, and on the Methods of Preparing it*," he explains the theory of the process as follows:—

"Manganese is an oxyd, a metal saturated with oxygen gas. Common salt is composed of muriatic acid and an alkaline salt called soda, the same which barilla affords. Manganese has greater affinity to sulphuric acid than to its oxygen, and the soda of the salt greater affinity to sulphuric acid than to the muriatic acid gas; hence it necessarily follows that these two gases (or rather their gravitating matter) must be liberated from their former union in immediate contact with each other; and although they have but a weak affinity to one another, they unite in their nascent state, that is to say, before they individually unite to caloric, and separately assume the gaseous state; for oxygen gas and muriatic acid gas already formed will not unite when mixed, in consequence principally of the distance at which their respective atmospheres of caloric keep their gravitating particles asunder. The compound resulting from these two gases still retains the property of assuming the gaseous state, and is the oxygenated muriatic gas."

Interesting as these views may appear, considering the time they were published, you will notice that the rôle played by the manganese in the process and the chemical nature of this substance were not at all understood. The law of multiple proportions had not yet been propounded by John Dalton, and the researches of Berzelius on the oxides of manganese were only published thirteen years later, in 1812. The green gas we are considering was still looked upon as muriatic acid to which oxygen had been added, in contradistinction to Scheele's view, who considered it as muriatic acid from which something, viz., phlogiston, had been abstracted.

It was Humphry Davy who had, by a series of brilliant investigations carried out in the Laboratory of the Royal Institution between 1808 and 1810, accumulated fact upon fact to prove that the gas hitherto called oxygenated muriatic acid did not contain oxygen. He announced in an historic paper, which he read before the Royal Society on July 12, 1810, his conclusion that this gas was an elementary body, which in muriatic acid was combined with hydrogen, and for which he proposed the name "*chlorine*,"

derived from the Greek *χλωρός*, signifying "green," the colour by which the gas is distinguished.

The numerous communications which Humphry Davy made to the Royal Society on this subject form one of the brightest and most interesting chapters in the history of chemistry. They have recently been reprinted by the Alembic Society, and I cannot too highly recommend their study to the young students of our science.

Those who have followed the history of chemistry I need not remind how hotly and persistently Davy's views were combated by a number of the most eminent chemists of his time, led by Berzelius himself; how long the chlorine controversy divided the chemical world; how triumphantly Davy emerged from it; how completely his views were recognised; and how very instrumental they have been in advancing theoretical chemistry.

The hope, however, which Davy expressed in that same historic paper, "that these new views would perhaps facilitate one of the greatest problems in economical chemistry, the decomposition of the muriates of soda and potash," was not to be realised so soon. Although it had changed its name, chlorine was still for many years manufactured by heating a mixture of salt, manganese, and sulphuric acid in leaden stills, as before.

This process leaves a residue consisting of sulphate of soda and sulphate of manganese, and for some time attempts were made to recover the sulphate of soda from these residues, and to use it for the manufacture of carbonate of soda by the Le Blanc process. On the other hand, the Le Blanc process, which had been discovered and put into practice almost simultaneously with Berthollet's chlorine process, decomposed salt by sulphuric acid, and sent the muriatic acid evolved into the atmosphere, causing a great nuisance to the neighbourhood.

Naturally, therefore, when Mr. William Gossage had succeeded in devising plant for condensing this muriatic acid, the manufacturers of chlorine reverted to the original process of Scheele, and heated manganese with the muriatic acid thus obtained. Since then the manufacture of chlorine has become a by-product of the manufacture of soda by the Le Blanc process, and remained so till very recently.

For a great many years the muriatic acid was allowed to act upon native ores of manganese in closed vessels of earthenware or stone, to which heat could be applied, either externally or internally. These native manganese ores, containing only a certain amount of peroxide, converted only a certain percentage of the muriatic acid employed into free chlorine, the rest combining with the manganese and iron contained in the ore, and forming a brown and very acid solution, which it was a great difficulty for the manufacturer to get rid of. Consequently, many attempts were made to regenerate peroxide of manganese from these waste liquors, so as to use it over again in the production of chlorine.

These, however, for a long time remained unsuccessful, because the exact conditions for super-oxidising the protoxide of manganese by means of atmospheric air were not yet known.

Meantime, viz., in 1845, Mr. Dunlop introduced into the works created by his grandfather, Mr. Charles Tennant, at St. Rollox, a new and very interesting method for producing chlorine, which was in a certain measure a return to the process used by the alchemists.

Indeed, the first part of this process consisted in decomposing a mixture of salt and nitre with oil of vitriol—a reaction that had been made use of for so many centuries! The chlorine so obtained is, however, not pure, but a mixture of chlorine with oxides of nitrogen and hydrochloric acid, which Mr. Dunlop had to find means to eliminate.

For separating the nitrous oxides Mr. Dunlop adopted the method introduced twenty years before by the great Gay-Lussac, in connection with vitriol-making, viz., absorption by sulphuric acid, and the nitro-sulphuric acid

thus formed he also utilised in the same way as that obtained from the towers which still bear Gay-Lussac's illustrious name, viz., by using it in the vitriol process in lieu of nitric acid. He then freed his chlorine gas from hydrochloric acid by washing with water, and so obtained it pure. This process possessed two distinct advantages—(1) It yielded a very much larger amount of chlorine from the same amount of salt, and (2) the nitric acid, which was used for oxidising the hydrogen in the hydrochloric acid, was not lost, because the oxides of nitrogen to which it was reduced answered the purpose for which the acid itself had previously been employed. But this process was very limited in its application, as it could only be worked to the extent to which nitric acid was used in vitriol-making.

The process has been at work at St. Rollox for over fifty years, and, as far as I know, is there still in operation; but I am not aware that it has ever been taken up elsewhere.

Within the last few years, however, several serious attempts have been made to give this process a wider scope by re-generating nitric acid from the nitro-sulphuric acid and employing it over and over again to convert hydrochloric acid into chlorine. Quite a number of patents have been taken out for this purpose, all employing atmospheric air for re-converting the nitrous oxides into nitric acid, and differing mainly in details of apparatus and methods of work, and several of these have been put to practical test on a fairly large scale in this neighbourhood, and also in Glasgow, Middlesbrough, and elsewhere. As I do not want to keep you here the whole afternoon, I have to draw the line somewhere as to what I shall include in this brief history of the manufacture of chlorine, and have had to decide to restrict myself to those methods which have actually attained the rank of manufacturing processes on a large scale. As none of the processes just referred to have attained that position, you will excuse me for not entering into further details respecting them.

Mr. Dunlop's process only produced a very small portion of the chlorine manufactured at that time at St. Rollox, the remainder being made, as before, from native manganese and muriatic acid, leaving behind the very offensive waste liquors I have mentioned before, which increased from year to year, and became more and more difficult to get rid of. The problem of recovering from these liquors the manganese in the form of peroxide Mr. Dunlop succeeded in solving in 1855.

He neutralised the free acid and precipitated the iron present by treating these liquors with ground chalk in the cold and settling out, and in later years, filter-pressing the precipitate, which left him a solution of chloride of manganese, mixed only with chloride of calcium. This was treated with a fresh quantity of milk of chalk, but this time under pressure in closed vessels provided with agitators and heated by steam, under which conditions all the manganese was precipitated as carbonate of manganese. This precipitate was filtered off and well drained, and was then passed on iron trays mounted on carriages through long chambers, in which it was exposed to hot air at a temperature of 300° C., the process being practically made continuous, one tray at the one end being taken out of these chambers, and a fresh tray being put in at the other end. One passage through these chambers sufficed to convert the carbonate of manganese into peroxide, which was used in place of, and in the same way as, the native manganese.

The whole of the residual liquors made at the large works at St. Rollox have been treated by this process with signal success for a long number of years. For a short time the process was discontinued in favour of the Weldon process (of which I have to speak next); but after two years Dunlop's process was taken up again, and to the best of my knowledge it is still in operation to this day. It has, however, just like Mr. Dunlop's first chlorine process, never left the place of its birth (St.

Rollox), although it was for a period of over ten years without a rival.

In 1866 Mr. Walter Weldon patented a modification of a process proposed by Mr. William Gossage in 1837 for recovering the manganese that had been used in the manufacture of chlorine. Mr. Gossage had proposed to treat the residual liquors of this manufacture by lime, and to oxidise the resulting protoxide of manganese by bringing it into frequent and intimate contact with atmospheric air. This process—and several modifications thereof subsequently patented—had been tried in various places without success. Mr. Weldon, however, did succeed in obtaining a very satisfactory result, possibly—even probably—because, not being a chemist, he did not add the equivalent quantity of lime to his liquor to precipitate the manganese, but used an excess. However, Mr. Weldon, if he was not a chemist at that time, was a man of genius and of great perseverance. He soon made himself a chemist, and having once got a satisfactory result, he studied every small detail of the reaction with the utmost tenacity until he had thoroughly established how this satisfactory result could be obtained on the largest scale with the greatest regularity and certainty.

He even went further, and added considerably to our theoretical knowledge of the character of manganese peroxide and similar peroxides by putting forward the view that these compounds possess the character of weak acids. He explained in this way the necessity for the presence of an excess of lime or other base if the oxidation of the precipitated protoxide of manganese by means of atmospheric air was to proceed at a sufficiently rapid rate. He pointed out that the product had to be considered as a manganite of calcium, a view which has since been thoroughly proved by the investigations of Goergen and others; and it is only fair to state that Weldon's process is not only a process for recovering the peroxide of manganese originally used, but that he introduced a new substance, viz., manganite of calcium, to be continuously used over and over again in the manufacture of chlorine.

Mr. Weldon had the good fortune that his ideas were taken up with fervency by Colonel Gamble of St. Helen's, and that Colonel Gamble's manager, Mr. F. Bramwell, placed all his experience as a consummate technical chemist and engineer at Mr. Weldon's disposal, and assisted him in carrying his ideas into practice. The result was that a process which many able men had tried in vain to realise for thirty years became, in the hands of Mr. Weldon and his coadjutors, within a few years, one of the greatest successes achieved in manufacturing chemistry.

The Weldon process commences by treating the residual liquor with ground chalk or limestone, thus neutralising the free acid and precipitating any sulphuric acid and oxide of iron present. The clarified liquor is run into a tall cylindrical vessel, and milk of lime is added in sufficient quantity to precipitate all the manganese in the form of protoxide. An additional quantity of milk of lime, from one-fifth to one-third of the quantity previously used, is then introduced, and air passed through the vessel by means of an air-compressor. After a few hours all the manganese is converted into peroxide; the contents of the vessel are then run off; the mud, now everywhere known as "Weldon mud," is settled, and the clear liquor run to waste. The mud is then pumped into large closed stone stills, where it meets with muriatic acid, chlorine is given off, and the residual liquor treated as before.

You note that this process works without any manipulation, merely by the circulation of liquids and thick magmas which are moved by pumping machinery. As compared to older processes it also has the great advantage that it requires very little time for completing the cycle of operations, so that large quantities of chlorine can be produced by a very simple and inexpensive plant.

These advantages secured for this process the quite unprecedented success that within a few years it was adopted, with a few isolated exceptions, by every large manufacturer of chlorine in the world; yet it possessed a distinct drawback, viz., that it produced considerably less chlorine from a given quantity of muriatic acid than either native manganese of good quality or Mr. Dunlop's recovered manganese. At that time, however, muriatic acid was produced as a by-product of the Le Blanc process so largely in excess of what could be utilised that it was generally looked upon as a waste product of no value. Mr. Weldon himself was one of the very few who foresaw that this state of things could not always continue. The ammonia soda process was casting its shadow before it. Patented in 1838 by Messrs. Dyar and Hemming, it was only after the lapse of thirty years (during which a number of manufacturing chemists of the highest standing had in vain endeavoured to carry it into practice) that this process was raised to the rank of a manufacturing process, through the indomitable perseverance of Mr. Ernest Solvay of Brussels, and his clear perception of its practical and theoretical intricacies. A few years later, in 1872, Mr. Weldon already gave his attention to the problem of obtaining the chlorine of the salt used in this process in the form of muriatic acid. He proposed to recover the ammonia from the ammonium chloride obtained in this manufacture by magnesia instead of lime, thus obtaining magnesium chloride instead of calcium chloride, and to produce muriatic acid from this magnesium chloride by a process patented by Clemm in 1863, viz., by evaporating the solution, heating the residue in the presence of steam, and condensing the acid vapours given off.

Strange to say, this same method had been patented by Mr. Ernest Solvay within twenty-four hours before Mr. Weldon lodged his specification. It has been frequently tried with many modifications, but has never been found practicable. Soon afterwards Mr. Weldon, with the object of reducing the muriatic acid required by his first process, proposed to replace the lime in this process by magnesia, and so to produce a manganite of magnesia. After treating this with muriatic acid and liberating chlorine, he proceeded to evaporate the residual liquors to dryness, during which operation all the chlorine they contain would be disengaged as hydrochloric acid and collected in condensers, while the dry residue, after being heated to dull redness in the presence of air, would be reconverted into manganite of magnesia.

This process was made the subject of long and extensive experiments at the works of Messrs. Gamble at St. Helen's, but did not realise Mr. Weldon's expectations. It, however, led to some further interesting developments, to which I shall refer later on.

Those of you who were present at the last meeting of the British Association in this city will remember that this Section had the advantage of listening to a paper by Mr. Weldon on his chlorine process, and also to another highly interesting paper by Mr. Henry Deacon of Widnes, "On a New Chlorine Process without Manganese." And those of you who came with the then President of the Section (Professor Roscoe) to Widnes, to visit the works of Messrs. Gaskell, Deacon, and Co., will well remember that at these works they saw, side by side, Weldon's process and Deacon's process in operation, and no one present will have forgotten the thoughtful flashing eyes and impressive face of Mr. Deacon when he explained to his visitors the theoretical views he had formed as regards his process.

Mr. Deacon had made a careful study of thermochemistry, which had been greatly developed during the preceding decade by the painstaking, accurate, and comprehensive experiments of Julius Thomsen and of Berthelot, and had led the latter to generalisations, which, although not fully accepted by scientific men, have been of immense service to manufacturing chemistry.

To be continued.)

LUCIUM, A NEW ELEMENT.

In the course of researches on monazite sand M. P. Barrière appears to have come upon a new elementary body, to which he has given the name *Lucium*, and which he purposes using for the production of an incandescent gas light in opposition to that of Auer von Welsbach.

Hence he has sought to show the new and independent character of lucium in order to prove that its use was not anticipated by the Welsbach patents. A careful examination led to the following results.

The chemical properties of lucium are as follows:—The salts of cerium, lanthanum, and didymium form with sodium sulphate insoluble double salts; lucium does not. Thorium and zirconium form insoluble double salts with potassium sulphate; this is not the case with lucium. Yttrium, ytterbium, and erbium are not precipitable by sodium thiosulphate, whilst lucium chloride is precipitable. From glucinium lucium differs, as its salts are precipitable by oxalic acid.

According to the results obtained by Prof. Schützenberger, confirmed by those of Cleve, Fresenius, and Lecoq de Boisbaudran, lucium dissolves in sulphuric, nitric, or acetic acid, forming salts either white or slightly tinted with rose-colour. All its salts are soluble in water, forming limpid, colourless solutions.

The spectral rays of lucium are special, and only approximate slightly to those of erbium. Erbium oxide, on ignition, appears of a very pure rose-colour, and its nitrate is red. On the contrary, lucium oxide is white, slightly greyish, and its nitrate is white. The aqueous solutions of the erbium salts are red or rose-colour; those of lucium, even if containing 15 or 20 per cent of the salt, are almost colourless.

The atomic weight of lucium is calculated as = 104, whilst—

Thorium	= 233
Yttrium	= 89
Ytterbium	= 173
Scandium	= 44.5
Cerium	= 140
Lanthanum	= 156
Erbium	= 166
Zirconium	= 90
Samarium	= 150
Glucinium	= 9

Hence the authorities cited regard lucium as a new, distinct elementary body.

THE INTRODUCTION OF STANDARD METHODS OF ANALYSIS.*

By the Baron HANNS JÜPTNER von JONSTORFF
(Neuberg, Austria).

(Continued from p. 144).

8. *The want of homogeneity of the sample* is one of the most important sources of error. It deserves most special attention in any case where it is a question of exhaustively testing analytical methods, since it is only when there is absolute certainty of the actual homogeneous composition of the material used in the parallel analyses that it is possible to obtain a trustworthy judgment upon the methods used.

This want of homogeneity of the sample is met with, however, in various ways. It is mostly shown in the varying composition of an ingot at the base or at the top, externally or internally. These are liquation phenomena, the results of which are very clearly shown in the following results of investigations by Snelus. From an ingot mea-

suring 19 by 19 by 84 inches, which was allowed to cool extremely slowly, he cut sections 4 inches above the base and 21 inches below the top, perpendicular to the axis, and from each of these sections he took six samples, No. 1 being at the corner, and No. 6 at the centre of the plate. The analyses gave the following results:—

No.	Top Plate.			Base Plate.		
	Carbon.	Silicon.	Phosphorus.	Carbon.	Silicon.	Phosph.
1	0.44	0.032	0.044	0.44	0.048	0.060
2	0.54	0.048	0.060	0.42	0.058	0.062
3	0.57	0.080	0.086	0.41	0.048	0.054
4	0.61	0.096	0.097	0.40	0.048	0.048
5	0.68	0.120	0.111	0.38	0.048	0.058
6	0.77	0.187	0.142	0.37	0.048	0.052

This want of homogeneity must obviously, also, be met with in the products obtained by cutting or rolling such ingots. Thus Eccles found that soft plates, of which the fracture at the two exterior sides was silky and in the centre granular, had the following composition:—

	Granular layer.	Silky portion.
	Per cent.	Per cent.
Carbon	0.160	0.175
Phosphorus	0.112	0.038
Sulphur	0.070	0.030
Manganese	0.570	0.576

A sheet 30 millimetres thick had the following composition:—

	Carbon.	Sulphur.	Phosphorus.	Manganese.
<i>Top End.</i>				
Exterior:—				
Longitudinal section	0.240	0.025	0.050	0.160
Cross section	0.240	0.017	0.052	0.150
Interior:—				
Longitudinal section	0.320	0.061	0.100	0.088
Cross section	0.400	0.070	0.088	0.140
<i>Bottom End.</i>				
Exterior:—				
Longitudinal section	0.250	0.028	0.060	0.120
Cross section	0.250	0.030	0.070	0.110
Interior:—				
Longitudinal section	0.250	0.022	0.060	0.120
Cross section	0.200	0.031	0.052	0.120

A. R. von Dormus (*Zeitschr. des Oesterr. Ingenieur und Architekten Vereins*, 1896, Nos. 13, 14, 15) gives the following interesting analyses of steel rails:—

No.	Point at which sample was taken.	C.	Si.	Mn.	P.	S.	Co.
358	Surface	0.411	0.011	0.477	0.063	0.026	0.130
"	Centre of head	0.525	0.007	0.506	0.104	0.038	0.126
"	Neck	0.485	0.010	0.506	0.099	0.040	0.123
"	Base	0.456	0.009	0.488	0.064	0.025	0.109
4185	Surface	0.396	0.013	0.500	0.063	0.033	0.131
"	Centre of head	0.480	0.014	0.494	0.089	0.041	0.152
"	Neck	0.456	0.009	0.500	0.079	0.037	0.130
"	Base	0.472	0.014	0.511	0.076	0.035	0.110
363	Surface	0.357	0.010	0.412	0.057	0.039	0.122
"	Centre of head	0.501	0.006	0.430	0.099	0.057	0.139
"	Neck	0.507	0.011	0.430	0.102	0.063	0.126
"	Base	0.459	0.014	0.407	0.063	0.033	0.105
4275	Surface	0.297	0.012	0.442	0.028	0.018	0.134
"	Centre of head	0.504	0.016	0.500	0.062	0.048	0.152
4164	Surface	0.387	0.008	0.494	0.027	0.017	0.134
"	Centre of head	0.441	0.007	0.506	0.046	0.027	0.137
5469	Surface	0.351	0.028	1.146	0.045	0.019	0.140
"	Centre of head	0.681	0.023	1.239	0.084	0.021	0.135

Portions immediately adjacent may, however, also exhibit a very variable composition. This is well known in the case of the carbon percentage of cement steel and of manufactured steel (being in the former greater at the surface, and in the latter less than in the interior), in the case of graphite (especially in mottled pig iron), and in

* Read before the Iron and Steel Institute.

that of slag (notably in weld iron). Other elements, such as manganese, phosphorus, and especially sulphur, may also, however, in certain circumstances, be very unequally distributed (*Oesterr. Zeitschr. für Berg- und Hüttenwesen*, 1896, p. 159). In the case of phosphorus determinations by eight different chemists, in one and the same pig iron, the highest result was about double as great as the lowest. In a pig iron sixteen chemists found, as is shown by the following figures (*Journ. Anal. and Applied Chem.*), from 0.005 to 0.024 per cent of sulphur, and the very highest and lowest of these results were obtained by chemists of high repute:—

	Sulphur, per cent.
a. Aqua regia method	0.005
b. Absorption and oxidation with bromine, treatment of the insoluble residue with aqua regia, barium sulphate precipitate weighed	0.008
c. Absorption and titration with normal iodine solution	0.009
d. Method not specified	0.010
e. Absorption in alkaline solution of lead nitrate and weighing the precipitate as barium sulphate	0.011
f. Aqua regia method; the solution was allowed to stand twenty-four hours after the addition of barium chloride	0.012
g. Aqua regia method	0.012
h. Absorption in potassium permanganate solution, and weighing the barium sulphate precipitate	0.013
Absorption in cadmium solution and titration with normal iodine solution	0.013
j. Potassium permanganate solution and barium sulphate weighed	0.013
k. Aqua regia method. Neutralised with ammonia. Precipitation of barium sulphate and allowed to stand for twenty-four hrs.	0.013
l. Absorption in cadmium chloride solution and titration with normal iodine solution	0.015
m. Absorption and titration with normal iodine solution	0.017
n. Absorption in potassium permanganate solution and weighing the barium sulphate	0.017
o. Volumetric analysis (details not specified)	0.019
p. Absorption in cadmium sulphate and titration with normal iodine solution	0.020
q. Aqua regia method	0.021
r. Absorption in caustic soda solution and titration with normal iodine solution	0.022
s. Aqua regia method	0.024

(To be continued).

ON THE AMOUNT OF GOLD AND SILVER IN SEA-WATER.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

(Continued from p. 148).

Southern Sea-waters.

In examining the southern sea-waters, in the first batch a litre of each was treated, and the characteristic reaction for gold obtained from Nos. 1, 2, 4, 5, 6. In the next batch of two litres each, 1, 2, 3, and 5 showed the presence of gold; the films were treated a second time with chlorine water, when Nos. 3, 4, and 5 gave the gold reaction. In the third batch, Nos. 1, 2, 3, and 6 reacted for gold, and on a second treatment Nos. 3 and 6 again gave the reaction for gold. The details are as follows:—

No. 1, South—Collected November 26, 1894, one mile east of South Head Lighthouse. Latitude 33° 43' S.

Test No. 1.—Upon 1 litre. SnCl_2 was added on Dec. 11, 1894, a white sediment was formed; this, on Feb. 8, 1895, had changed to a slate colour; the slate colour was probably due to the presence of gold.

Test No. 2.—Upon 2 litres. December 22, 1894, the white precipitate on February 8, 1895, showed a pinkish ring at upper part, evidently due to the presence of gold. The film from the ferrous sulphate was extracted a second time with Cl water, on December 31; the solution became opalescent on the addition of the HCl and SnCl_2 , and acquired a bluish tinge (probably due to gold), but by February 8 this blue tint had disappeared and only a white sediment remained.

Test No. 3.—Upon 1500 c.c. June 12, 1895. On June 21 the white precipitate showed a pinkish layer at the top $\frac{1}{8}$ inch deep, the pink colour was more decided on the 24th. On July 3 and 4 it began to turn violet, and on July 7 was of a distinct violet tint, and on July 10 the upper part of the precipitate had darkened to a purple colour, which was doubtless due to the presence of gold.

No. 2, South—Collected November 26, 1894, three miles off Bulli. Latitude about 34°.

Test No. 1.—Gave a slight white sediment; on Feb. 8 this was yellowish with a dark reddish brown ring.

Test No. 2.—On 2 litres. Put up on December 22, 1894. On December 31 the sediment was white; but had acquired a pinkish tinge on the surface by February 8, 1895. The iron oxide film was extracted a second time with Cl water on December 31; this gave a brownish coloured solution and a white precipitate, which had not changed by February 8.

Test No. 3.—Upon 1500 c.c. June 12, 1895. On July 6 there was a slight red tint on the sediment, and on July 10 this had become brown.

No. 3, South—Collected November 27, 1894, five miles from Black Head, Shoalhaven Bight. Latitude about 34°.

Test No. 1.—Upon 1 litre. Clear bluish tinge, sediment slightly coloured.

Test No. 2.—On 2 litres. A slight amethyst tint within three minutes after adding the SnCl_2 . On February 8, 1895, the sediment was bluish below with the pink colour above unchanged. The second Cl water extract of the film, on adding the SnCl_2 , became opalescent with a faint amethyst tinge; on February 8, 1895, the sediment was white with light reddish brown ring.

Test No. 3.—1900 c.c. June 21, 1895. A buff sediment with a pinkish tint at top; on the 24th the pink tint was deeper, a pale violet on July 3, and on July 6 had become a full violet; on July 10 this had become purple—the buff below remaining unchanged.

No. 4, South—Collected November 27, 1894, from one mile off Cape St. George Lighthouse, Jervis Bay. Latitude about 35° S.

Test No. 1.—Upon 1 litre. December 11, 1894. After standing 5 hours the solution was clear with a bluish tinge; sediment slightly coloured. On February 8, 1895, the white sediment was marked by a reddish ring.

Test No. 2.—Two litres, on December 22, 1894. No colour on the 29th nor on February 8, 1895. Nor from the second Cl water extract; afterwards yielded a bluish tinge with pinkish colour to sediment.

Test No. 3.—1900 c.c. June 21, 1895. A bluish tinge on top of white sediment observed July 5, 1895.

No. 5, South—Collected November 27, 1894, from two miles off Brush Island. Latitude about 35° 5' S.

Test No. 1.—Upon 1 litre. December 11, 1894. Clear bluish tinge; on February 8, 1895, the white sediment showed a bright pink ring.

Test No. 2.—Gave no indication of gold, neither did the second Cl water extract.

* Read before the Royal Society of N. S. Wales.

Test No. 3.—1300 c.c. June 21, 1895. On addition of the stannous chloride this gave a bluish tinge; on July 10 the white sediment was almost black at the base.

No. 6, South—Collected November 28, 1894. From twenty-seven miles off Broulee, near Moruya. Latitude about $36^{\circ} 5' S$.

Test No. 1.—Upon 1 litre. December 11, 1894. No colour until February 8, 1895, when the light brown sediment showed a reddish ring.

Test No. 2.—Upon 2 litres. Amethyst tinge. Second extract with Cl water gave a bluish tinge and the sediment had a slight pink colouration.

Test No. 3.—1225 c.c. June 21, 1895. On June 24 the white sediment showed a pink tinge at top one-sixteenth inch deep; on July 10, 1895, the sediment was pale brown with an onyx-like layer near the top, with faint purple tinge.

On April 3, 1895, the precipitate in each test-tube of the first batch of southern waters had changed to a dirty, almost black, colour, *i.e.*, after an interval of nearly four months from the initiation of the experiment, *viz.*, from December 18, 1894, to April 3, 1895.

It was noticed, in some instances, that after long standing the pink or violet tint gradually faded, especially on the side exposed to the brighter light of the window; in some cases the colour disappeared totally.

Northern Sea-waters.

No. 1.—Collected February 19th, 1895, about $1\frac{1}{2}$ miles off Sandy Point, Richmond River, Lat. about $28^{\circ} S$.

No. 2.—Collected at North Solitary, Lat. about $29^{\circ} S$, February 19th, a strong southerly current.

No. 3.—From about 4 miles off Smoky Cape, Lat. about 30° , on February 20th.

No. 4.—From 2 miles off Tacking Point, Lat. about $31^{\circ} 30'$, February 20th.

No. 5.—From 2 miles off Cape Hawke, Lat. about $32^{\circ} 2'$, February 20th.

No. 6.—About 5 miles off Port Stephens, Lat. about 33° , February 20th.

All six samples of northern sea-waters also gave the reaction for gold; the details are omitted for brevity. As in the case of the southern samples, some gave the reaction readily, others required from one to several weeks. I should not, however, like to say that this is a sufficient indication of some being richer than others, for the test appears to be wanting in precision.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 9, August 31, 1896.

Doubling Back of the X Rays behind Opaque Bodies.—Emile Villari.—When studying the transparency of metals to the X rays I interposed leaves of them between a pear-shaped Crookes tube and a charged electro-scope. In numerous experiments I observed that the electro-scope was always discharged, even if it was placed in the full shadow of the rays produced by ample metallic screens, perfectly opaque. This fact made me suppose that the rays, or their efficiency, were doubled back in the shadow of opaque bodies so as to strike the electro-scope and discharge it. From further experiments it resulted that, to discharge the electro-scope it is not necessary that it should be struck directly by the X rays, since it is sufficient if the air which has been traversed by them arrives there. In fact, the electro-scope is rapidly discharged from 10° in twenty-eight seconds, if the air

which has been traversed by the rays is driven against it by means of a blast. On the contrary, when the Crookes tube is inactive the air driven against the electro-scope exerts no action. Therefore we may say that the X rays give to air the activity necessary to discharge the electro-scope—an activity which is preserved for a certain time.

Researches on Double Chlorides.—Raoul Varet.—The compounds formed by mercuric chloride when uniting with other metallic chlorides have, in the dissolved state, formation heats which are of the same order of magnitude for one and the same series of double salts. The formation of compounds produced by the chlorides of kindred metals give rise therein to effects which are sensibly equal. Dialysis shows that these combinations are partly dissociated in the midst of their solutions. These data lead us to regard these double salts as being derivatives of sparingly stable complex acids, such as $Hg_2Cl_6H_2$ and $HgCl_4H_2$. The double salts formed by the chlorides of copper, cadmium, &c., are dissociated by dialysis. Their formation in the dissolved state only gives rise to very feeble thermic effects.

Action of the Soluble Oxidising Ferment of Mushroom upon Phenols Insoluble in Water.—Emile Bourquelot.—Three xlenols have been tried, dissolved in 0.50 gm. of absolute alcohol and 50 c.c. of water. With orthoxlenol there was produced a white precipitate turning to a salmon colour. With metaxlenol the precipitate was also white, becoming a dirty rose. The precipitate dissolves in ether with a deep yellow colour. With paraxlenol there is produced a rosy white precipitate, insoluble in ether. Naphthols α and β are also oxidised. Naphthol α colours the liquid violet, passing then to blue, and then forming a dirty blue precipitate. The precipitate is partially stable in ether, with a mauve colour. With naphthol β there is formed a white precipitate, which gradually turns yellow. This precipitate is almost entirely soluble in ether, which takes a deep yellow colour.

Congelation-point of Cows' Milk.—MM. Bordas and Génin.—Some chemists have asserted that the congelation-point of milk is constant, so that the addition of water can thus be detected. The authors, on the contrary, find that the congelation-point of milk is variable and cannot be used to detect sophistication with water.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) at the Liverpool Meeting of the British Association:—

President—Dr. Ludwig Mond, F.R.S.

Vice-Presidents—Sir F. Abel, F.R.S.; Prof. J. Campbell Brown; Prof. J. Dewar, F.R.S.; Dr. J. H. Gladstone, F.R.S.; Dr. A. G. Vernon Harcourt, F.R.S.; Prof. R. Meldola, F.R.S.; E. K. Muspratt; Prof. W. Ramsay, F.R.S.; Sir H. E. Roscoe, F.R.S.; Dr. T. E. Thorpe, F.R.S.

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The Papers brought before the Section were as follows:—

President's Address.

Prof. H. B. Dixon—Reflected Waves in the Explosion of Gases.

Dr. J. H. Gladstone and W. Hibbert—Action of Metals and their Salts on the Ordinary and Röntgen Rays: a Contrast.

Prof. F. Clowes—Limiting Explosive Proportions of Acetylene, and Detection and Measurement of the Gas in the Air.

Prof. F. Clowes—The Accurate Determination of Oxygen by Absorption with Alkaline Pyrogallol Solution.

Dr. A. W. Titherley—The Amides of the Alkali Metals and some of their Derivatives.

D. H. Nagel—Report of the Committee on the Bibliography of Spectroscopy.

Prof. J. Hummel—Report of the Committee on the Action of Light on Dyed Colours.

C. F. Cross—Report of the Committee on the Carbohydrates of Barley Straw.

Prof. Oscar Liebreich—Diminution of Chemical Action resulting from Limitations of Space.

Prof. M. Bamberger—Excrement Resins.

Prof. P. P. Bedson—Report of the Committee to Inquire into the Proximate Chemical Constituents of the various kinds of Coal.

Dr. M. Wildermann—The Velocity of Reactions before perfect Equilibrium takes place.

Dr. T. Bradshaw—The Behaviour of Litmus in Amphoteric Solutions.

A. G. Green and A. Wahl—Constitution of Sun Yellow or Curcumine and Allied Colouring Matters.

Dr. F. E. Francis—Abnormalities in the Behaviour of Ortho-derivatives of *o*-Amido and Nitro-benzylamine.

Dr. W. Newton—Nitrates: their Occurrence and Manufacture.

Prof. Ramsay—Helium.

Prof. M. Bamberger—The presence of Argon in the Gases of an Austrian Well.

Dr. F. Hurter—The Manufacture of Chlorine by means of Nitric Acid.

Prof. J. Dewar—Low Temperature Research.

Report of the Committee on Electrolytic Analysis.

Dr. C. A. Kohn—A Modified Form of Schröter's Apparatus.

Dr. C. A. Kohn and Dr. T. L. Bailey—A New Form of Aspirator.

Dr. J. Haldane—The Detection and Estimation of Carbon Monoxide in Air.

Prof. F. Clowes—Detection of Minute Quantities of Carbon Monoxide by the Flame-cap Test.

Sir H. E. Roscoe—Chemical Education in England and Germany.

Dr. J. H. Gladstone—Report of the Committee on the Teaching of Science in Elementary Schools.

L. Edna Walter—The Teaching of Science in Girls' Schools.

Separation of Bismuth from the Metals of the Copper and the Iron Group by Heating their Salts in a Current of Dry Hydrochloric Acid.—*P. Jannasch and S. Grosse* (a Preliminary Communication).—In carrying out a great number of separations of arsenic from the metals of the copper and the iron group, of which we shall give account on opportunity, we made the observation that bismuth also, under suitable experimental conditions, can be easily and completely volatilised from mixtures of metallic salts, in a current of dry hydrochloric acid, at a relatively low temperature, thus showing a behaviour quite analogous to that of tin. This fact, as we have established, renders it possible to separate bismuth quantitatively from a series of less readily volatile metallic chlorides. We have already taken in hand analyses of this kind.—*Zeitsch. f. Anorganische Chemie*, vol. xii., Part 5, p. 398.

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VOL. LXXIV., No. 1923.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

LIVERPOOL, 1896.

By Dr. LUDWIG MOND, F.R.S., President of the Section.

(Concluded from p. 158).

MR. DEACON came to the conclusion that if a mixture of hydrochloric acid with atmospheric air was heated in the presence of a suitable substance capable of initiating the interaction of these two gases by its affinity to both, it would to a very great extent be converted into chlorine with the simultaneous formation of steam, because the formation of steam from oxygen and hydrogen gives rise to the evolution of a considerably larger quantity of heat than the combination of hydrogen and chlorine. Mr. Deacon found that the salts of copper were a very suitable substance for this purpose, and took out a patent for this process in 1868. He entrusted the study of the theoretical and practical problems connected with this process to Dr. Ferdinand Hurter, who carried them out in a manner which will always remain memorable and will never be surpassed, as an example of the application of scientific methods to manufacturing problems, and which soon placed this beautiful and simple process on a sound basis as a manufacturing operation.

In the ordinary course of manufacture the major part—about two-thirds—of the hydrochloric acid is obtained mixed with air and a certain amount of steam, but otherwise very little contaminated. Instead of condensing the muriatic acid from this mixture of gases by bringing it into contact with water, Mr. Deacon passed it through a long series of cooling pipes to condense the steam, which of course absorbed hydrochloric acid, and formed a certain quantity of strong muriatic acid. The mixture of gases was then passed through an iron superheater to raise it to the required temperature, and thence through a mass of broken bricks impregnated with sulphate or chloride of copper contained in a chamber or cylinder called a decomposer, which was protected from loss of heat by being placed in a brick furnace kept sufficiently hot. In this apparatus from 50 to 60 per cent of the hydrochloric acid in the mixture of gases was burnt to steam and chlorine. In order to separate this chlorine from the steam and the remaining hydrochloric acid the gases were washed with water, and subsequently with sulphuric acid. The mixture now consisted of nitrogen and oxygen, containing about 10 per cent of chlorine gas, which could be utilised without any difficulty in the manufacture of bleach liquors and chlorate of potash, and which Mr. Deacon also succeeded in using for the manufacture of bleaching powder, by bringing it into contact in specially constructed chambers with large surfaces of hydrate of lime. Within recent years this latter object has been attained in a more expeditious and perfect manner by continuous mechanical apparatus (of which those constructed by Mr. Robert Hasenclever and Dr. Carl Langer have been the most successful), in which the hydrate of lime is transported in a continuous stream by single or double conveyors in an opposite direction to the current of dilute chlorine, and the bleaching powder formed delivered direct into casks, thereby avoiding the intensely disagreeable work of packing this offensive substance by hand.

Mr. Deacon's beautiful and scientific process thus involves still less movement of materials than the very simple process of Mr. Weldon, because, in lieu of large volumes of liquids, he only moves a current of gas through

his apparatus, which requires a minimum of energy. The only raw material used for converting hydrochloric acid into chlorine is atmospheric air, the cheapest of all at our command. The hydrochloric acid which has not been converted into chlorine by the process is all obtained, dissolved in water, as muriatic acid, and is not lost, as in previous processes, but is still available to be converted into chlorine by other methods, or to be used for other purposes.

In spite of these distinct advantages, this process took a long time before it became adopted as widely as it undoubtedly deserved. This was mainly due to the fact that the economy in the use of muriatic acid which it effected was at the time when the process was brought out, and for many years afterwards, no object to the majority of chlorine manufacturers, who were still producing more of this commodity than they could use. Moreover, there were other reasons. The plant required for this process, although so simple in principle, is very bulky in proportion to the quantity of chlorine produced, and, as I have pointed out, the process only succeeded in converting about one-third of the hydrochloric acid produced into chlorine, the remainder being obtained as muriatic acid, which had in most instances to be converted into chlorine by the Weldon process; so that the Deacon process did not constitute an entirely self-contained method for this manufacture. This defect, of small moment as long as muriatic acid was produced in excessive quantities, was only remedied by an invention of Mr. Robert Hasenclever a short number of years ago; when by the rapid development of the ammonia soda process the previously existing state of things had been completely changed, and when, at least on the Continent, muriatic acid was no longer an abundant and valueless by-product, but, on the contrary, the alkali produced by the Le Blanc process had become a by-product of the manufacture of chlorine. Mr. Hasenclever, in order to make the whole of the muriatic acid he produces available for conversion into chlorine by the Deacon process, introduces the liquid muriatic acid in a continuous stream into hot sulphuric acid contained in a series of stone vessels, through which he passes a current of air. He thus obtains a mixture of hydrochloric acid and air, well adapted for the Deacon process, the water of the muriatic acid remaining with the sulphuric acid, from which it is subsequently eliminated by evaporation. In this way the chlorine in the hydrochloric acid can be almost entirely obtained in its free state by the simplest imaginable means, and with the intervention of no other chemical agent than atmospheric air. Since their introduction the Deacon process has supplanted the Weldon process in nearly all the largest chlorine works in France and Germany, and is now also making very rapid progress in this country.

Mr. Weldon, when he decided to give up his manganite of magnesia process, by no means relaxed his efforts to work out a chlorine process which should utilise the whole of the muriatic acid. While working with manganite of magnesia he found that magnesia alone would answer the purpose without the presence of the peroxide of manganese. He obtained the assistance of M. Pechiney, of Salindres, and in conjunction with him worked out what has become known as the "Weldon-Pechiney" process, which was first patented in 1884.

This process consists in neutralising muriatic acid by magnesia, concentrating the solution to a point at which it does not yet give off any hydrochloric acid, and then mixing into it a fresh quantity of magnesia so as to obtain a solid oxychloride of magnesium. This is broken up into small pieces, which are heated up rapidly to a high temperature without contact with the heating medium, while a current of air is passing through them. The oxychloride of magnesium containing a large quantity of water, this treatment yields a mixture of chlorine and hydrochloric acid with air and steam, the same as the Deacon process, and this is treated in a very similar way

to eliminate the steam and the acid from the chlorine. The acid condensed is, of course, treated with a fresh quantity of magnesia, so that the whole of the chlorine which it contains is gradually obtained in the free state.

The rapid heating to a high temperature of the oxy-chloride of magnesium without contact with the heating medium was an extremely difficult practical problem, which has been solved by M. Pechiney and his able assistant, M. Boulouvard, in a very ingenious and entirely novel way.

They lined a large wrought-iron box with fire-bricks, and built inside of this vertical fire-brick walls with small empty spaces between them, thus forming a number of very narrow chambers, so arranged that they could all be filled from the top of the box and emptied from the bottom. These chambers they heated to a very high temperature by passing a gas flame through them, thus storing up in the brick walls enough heat to carry out and complete the decomposition of the magnesium oxy-chloride, with which the chamber was filled when hot enough.

Mr. Weldon himself called this apparatus a "baker's oven," in which trade certainly the same principle has been employed from time immemorial; but to my knowledge it had never before been used in any chemical industry. This process has been at work at M. Pechiney's large alkali works at Salindres, and is now at work in this country at the chlorate of potash works of Messrs. Allbright and Wilson at Oldbury, a manufacture for which it offers special advantages. Mr. Weldon and M. Pechiney had expected that this process would become specially useful in connection with the ammonia soda process by preparing, in the way proposed by Mr. Solvay and Mr. Weldon in 1872, a solution of magnesium chloride as a by-product of this manufacture; but instead of obtaining muriatic acid from this solution by Clemm's process, to treat it by the new process, so as to obtain the bulk of the chlorine at once in the free state. But M. Pechiney did no more succeed than his predecessors in recovering the ammonia by means of magnesia in a satisfactory way.

Quite recently, however, it has been applied to obtain chlorine in connection with the ammonia soda process by Dr. Pick, of Czakowa, in Austria. He recovers the ammonia, as usual, by means of lime, and converts the solution of chloride of calcium, obtained by a process patented by Mr. Weldon in 1869, viz., by treatment with magnesia and carbonic acid under pressure, into chloride of magnesium with the formation of carbonate of lime. The magnesium chloride solution is then concentrated and treated by the Weldon-Pechiney process.

I have repeatedly referred during this brief history to the great change which has been brought about in the position of chlorine manufacture by the development of the ammonia soda process, and have pointed out that the muriatic acid which for a long time was the by-product of the Le Blanc process, without value, thereby became gradually its main and most valuable product, while the alkali became its by-product.

I have told you how, very early in the history of this process, Mr. Solvay and Mr. Weldon proposed means to provide for this contingency, and how Mr. Weldon continued to improve these means until the time of his death. Mr. Solvay, on his part, also followed up the subject with that tenacity and sincerity of purpose which distinguishes him, his endeavours being mainly directed to producing chlorine direct from the chloride of calcium running away from his works by mixing it with clay and passing air through the mixture at very high temperatures, thus producing chlorine and a silicate of calcium, which could be utilised in cement-making. The very high temperatures required prevented, however, this process from becoming a practical success.

I have already told you what a complicated series of operations Dr. Pick has lately resorted to in order to obtain the chlorine from this chloride of calcium. Yet the problem of obtaining chlorine as a by-product of

the ammonia soda process presents itself as a very simple one.

This process produces a precipitate of bicarbonate of soda and a solution of chloride of ammonium by treating natural brine or an artificially made solution of salt, in which a certain amount of ammonia has been dissolved, with carbonic acid. In their original patent of 1838 Messrs. Dyar and Herring proposed to evaporate this solution of ammonium chloride, and to distil the resulting dry product with lime to recover the ammonia. Now all that seemed to be necessary to obtain the chlorine from this ammonium chloride was to substitute another oxide for lime in the distillation process, which would liberate the ammonia and form a chloride which on treatment with atmospheric air would give off its chlorine and reproduce the original oxide. The whole of the reactions for producing carbonate of soda and bleaching powder from salt would thus be reduced to their simplest possible form; the solution of salt, as we obtain it in the form of brine direct from the soil, would be treated with ammonia and carbonic acid to produce bicarbonate and subsequently monocarbonate of soda, the limestone used for producing the carbonic acid would yield the lime required for absorbing the chlorine, and produce bleaching powder instead of being run into the rivers in combination with chlorine in the useless form of chloride of calcium, and both the ammonia used as an intermediary in the production of soda and the metallic oxide used as an intermediary in the production of chlorine would be continuously recovered.

The realisation of this fascinating problem has occupied me for a great many years. In the laboratory I obtained soon almost theoretical results. A very large number of oxides and even of salts of weak acids were found to decompose ammonium chloride in the desired way; but the best results (as was to be clearly anticipated from thermo-chemical data) were given by oxide of nickel.

When, however, I came to carry this process out on a large scale, I met with the most formidable difficulties, which it took many years to overcome successfully.

The very fact that ammonium chloride vapour forms so readily metallic chlorides when brought in contact at an elevated temperature with metals or oxides, or even silicates, led to the greatest difficulty, viz., that of constructing apparatus which would not be readily destroyed by it.

Amongst the metals we found that platinum and gold were the only ones not attacked at all. Antimony was but little attacked, and nickel resisted very well if not exposed to too high a temperature, so that it could be, and is being, used for such parts of the plant as are not directly exposed to heat. The other parts of the apparatus coming in contact with the ammonium chloride vapour I ultimately succeeded in constructing of cast and wrought iron, lined with fire-bricks or Doulton tiles, the joints between these being made by means of a cement consisting of sulphate of baryta and water-glass.

After means had been devised for preventing the breaking of the joints through the unequal expansion of the iron and the earthenware, the plant so constructed has lasted very well.

Oxide of nickel, which had proved the most suitable material for the process in the laboratory, gave equally good chemical results on the large scale, but occasionally a small quantity of nickel chloride was volatilised through local over-heating, which, however, was sufficient to gradually make up the chlorine conduits. We therefore looked out for an active material free from this objection. Theoretical considerations indicated magnesia as the next best substance, but it was found that the magnesium chloride formed was not anhydrous, but retained a certain amount of the steam formed by the reaction, which gave rise to the formation of a considerable quantity of hydrochloric acid on treatment with hot air. In conjunction with Dr. Eschellman (who carried out the experiments

for me), I succeeded in reducing the quantity of this hydrochloric acid to a negligible amount by adding to the magnesia a certain amount of chloride of potassium, which probably has the effect of forming an anhydrous double chloride.

This mixture of magnesia and potassium chloride is, after the addition of a certain quantity of china clay, made into small pills, in order to give a free and regular passage throughout their entire mass to the hot air and other gases with which they have to be treated. In order to avoid as far as possible the handling and consequent breaking of these pills, I vapourise the ammonium chloride in a special apparatus, and take the vapours through these pills and subsequently pass hot air through, and then again ammonium chloride vapour, and so on, without the pills changing their place.

The vapourisation of the ammonium chloride is carried out in long cast-iron retorts lined with thin Doulton tiles, and placed almost vertically in a furnace which is kept by producer gas at a very steady and regular temperature. These retorts are kept nearly full with ammonium chloride, so as to have as much active heating surface as possible. From time to time a charge of ammonium chloride is introduced through a hopper at the top of these retorts, which is closed by a nickel plug. The ammonium chloride is very pure, being crystallised out from its solution as produced in the ammonia soda manufacture by a process patented by Mr. Gustav Jarmay, which consists in lowering the temperature of these solutions considerably below 0°C . by means of refrigerating machinery. The retorts will therefore evaporate a very large amount of ammonium chloride before it becomes necessary to take out through a door at their bottom the non-volatile impurities which accumulate in them. The ammonium chloride vapour is taken from these retorts by cast-iron pipes lined with tiles and placed in a brick channel, in which they are kept hot, to prevent the solidification of the vapour, to large upright wrought-iron cylinders which are lined with a considerable thickness of fire-bricks, and are filled with the magnesia pills, which are, from the previous operations, left at a temperature of about 300°C . On its passage through the pills the chlorine in the vapours is completely retained by them, the ammonia and water vapour formed pass on and are taken to a suitable condensing apparatus. The reaction of the ammonium chloride vapour upon magnesia being exo-thermic, the temperature of the pills rises during this operation, and no addition of heat is necessary to complete it. The temperature, however, does not rise sufficiently to satisfactorily complete the second operation, viz., the liberation of the chlorine and the re-conversion of the magnesium chloride into magnesium oxide by means of air. This reaction is slightly endo-thermic, and thus absorbs a small amount of heat, which has to be provided in one way or another. I effect this by heating the pills to a somewhat higher temperature than is required for the action of the air upon them, viz., to 600°C ., by passing through them a current of a dry inert gas free from oxygen, heated by a Siemens-Cowper stove to the required temperature. I use for this purpose the gas leaving the carbonating plant of the ammonia soda process.

This current of gas also carries out of the apparatus the small amount of ammonia which was left in between the pills. It is washed to absorb this ammonia, and, after washing, this same gas is passed again through the Siemens-Cowper stove, and thus constantly circulated through the apparatus, taking up the heat from the stove and transferring it to the pills. When these have attained the required temperature, the hot inert gas is stopped and a current of hot air passed through, which has also been heated to 600°C . in a similar stove. The air acts rapidly upon the magnesium chloride, and leaves the apparatus charged with 18 to 20 per cent of chlorine and a small amount of hydrochloric acid. The chlorine comes gradually down, and when it has reached about 3 per cent

the temperature of the air entering the apparatus is lowered to 350°C . by the admixture of cold air to the hot air from the stove; and the weak chlorine leaving the apparatus is passed through a second stove, in which its temperature is raised again to 600°C ., and passed into another cylinder full of pills which are just ready to receive the hot-air current. A series of four cylinders is required to procure the necessary continuity for the process.

The chlorine gas is washed with a strong solution of chloride of calcium, which completely retains all the hydrochloric acid, and is then absorbed in an apparatus invented by Dr. Carl Langer, by hydrate of lime, which is made to pass by a series of interlocked transporting twin-screws in an opposite direction to the current of gas, and produces very good and strong bleaching powder, in spite of the varying strength of the chlorine gas. The hydrochloric acid absorbed by the solution of calcium chloride can, by heating this solution, be readily driven out and collected.

This process has now been in operation on a considerable scale at our works at Winnington for several years, with constantly improving results, notably with regard to the loss of ammonia, which has gradually been reduced to a small amount. The process has fully attained my object, viz., to enable the ammonia soda process to compete not only in the production of carbonate of soda, but also in the production of bleaching powder, with the *Le Blanc* process.

Nevertheless, I have hesitated to extend this process as rapidly as I should otherwise have done, because, very shortly after I had overcome all its difficulties, entirely different methods from those hitherto employed for the manufacture of chlorine were actively pushed forward in different parts of the globe, for which great advantages were claimed, but the real importance and capabilities of which were—and are up to this date—very difficult to judge. I refer to the processes for producing chlorine by electrolysis.

During the first decade of this century Humphry Davy had, by innumerable experiments, established all the leading facts concerning the decomposing action of an electric current upon chemical compounds. Amongst these he was the first to discover that solutions of alkaline chlorides, when submitted to the action of a current, yield chlorine. His successor at the Royal Institution, Michael Faraday, worked out and proved the fundamental law of electrolysis, known to everybody as "*Faraday's Law*," which has enabled us to calculate exactly the amount of current required to produce by electrolysis any definite quantity of chlorine. Naturally, since these two eminent men had so clearly shown the way, numerous inventors have endeavoured to work out processes based on these principles for the production of chlorine on a manufacturing scale, but only during the last few years have these met with any measure of success.

It has taken all this time for the classical work of Faraday on electro-magnetism to develop into the modern magneto-electric machine, capable of producing electricity in sufficient quantity to make it available for chemical operations on a large scale; for you must keep in mind that an electric installation sufficient to light a large town will only produce a very moderate quantity of chemicals.

In applying electricity to the production of chlorine, various ways have been followed, both as to the raw materials and as to the apparatus employed. While most inventors have proposed to electrolyse a solution of chloride of sodium, and to produce thereby chlorine and caustic soda, I am not aware that up to this day any quantity of caustic soda made by electrolysis has been put on to the market.

Only two electrolytic works producing chlorine on a really large scale are in operation to-day. Both electrolyse chloride of potassium, producing as a by-product caustic potash, which is of very much higher value than

caustic soda, and of which a larger quantity is obtained for the same amount of current expended. These works are situated in the neighbourhood of Stassfurt, the important centre of the chloride of potassium manufacture. The details of the plant they employ are kept secret, but it is known that they use cells with porous diaphragms of special construction, for which great durability is claimed. There are at this moment a considerable number of smaller works in existence, or in course of erection in various countries, intended to carry into practice the production of chlorine by electrolysis by numerous methods, differing mainly in the details of the cells to be used, but some of them also involving what may be called new principles. The most interesting of these are the processes in which mercury is used alternately as cathode and anode, and salt as electrolyte. They aim at obtaining in the first instance chlorine and an amalgam of sodium, and subsequently converting the latter into caustic soda by contact with water, which certainly has the advantage of producing a very pure solution of caustic soda. Mr. Hamilton Castner has carried out this idea most successfully by a very beautiful decomposing cell, which is divided into various compartments, and so arranged that by slightly rocking the cell the mercury charged with sodium in one compartment passes into another, where it gives up the sodium to water, and then returns to the first compartment to be re-charged with sodium. His process has been at work on a small scale for some time at Oldbury, near Birmingham, and works for carrying it out on a large scale are now being erected on the banks of the Mersey, and also in Germany and America.

Entirely different from the foregoing, but still belonging to our subject, are methods which propose to electrolyse the chlorides of heavy metals (zinc, lead, copper, &c.) obtained in metallurgical operations or specially prepared for the purpose, among which the processes of Dr. Carl Hoepfner deserve special attention. They eliminate from the electrolyte immediately both the products of electrolysis, chlorine on one side and zinc and copper on the other, and thus avoid all secondary reactions, which have been the great difficulty in the electrolysis of alkaline chlorides.

All these processes have, however, still to stand the test of time before a final opinion can be arrived at as to the effect they will have upon the manufacture of chlorine, the history of which we have been following, and this must be my excuse for not going into further details. I have endeavoured to give you a brief history of the past of the manufacture of chlorine, but I will to-day not attempt to deal with its future! Yet I cannot leave my subject without stating the remarkable fact that every one of these processes which I have described to you is still at work to this day, even those of Scheele and Berthollet, all finding a sphere of usefulness under the widely varying conditions under which the manufacture of chlorine is carried on in different parts of the world.

Let me express a hope that a hundred years hence the same will be said of the processes now emerging and the processes still to spring out of the inventor's mind. Rapid and varied as has been the development of this manufacture, I cannot suppose that its progress is near its end, and that Nature has revealed to us all her secrets as to how to procure chlorine with the least expenditure of trouble and energy. I do not believe that industrial chemistry will in future be diverted from this Section and have to wander to Section A under theegis of applied electricity. I do not believe that the easiest way of effecting chemical changes will ultimately be found in transforming heat and chemical affinity into electricity, tearing up chemical compounds by this powerful medium, and then to re-combine their constituents in such form as we may require them. I am sure there is plenty of scope for the manufacturing chemist to solve the problems before him by purely chemical means, of some of which we may as little dream to-day as a few years ago it could

have been imagined that nickel would be extracted from its ores by means of carbon monoxide.

At a meeting of this Association which brings before us an entirely new form of energy, the Röntgen rays, which have enabled us to see through doors and walls, and to look inside the human body: which brings before us a new form of matter, represented by argon and helium, which, as their discoverers, Lord Rayleigh and Professor Ramsay, have now abundantly proved, are certainly elementary bodies, inasmuch as they cannot be split up further, but are not chemical elements, as they possess no chemical affinity and do not enter into combinations,—at a meeting at which such astounding and unexpected secrets of Nature are revealed to us, who would call in doubt that, notwithstanding the immense progress pure and applied science have made during this century, new and greater and farther-reaching discoveries are still in store for ages to come?

ON THE AMOUNT OF GOLD AND SILVER IN SEA-WATER.*

By A. LIVERSIDGE, M.A., F.R.S.,
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(Concluded from p. 161).

Quantitative Tests.

UNFORTUNATELY all the samples had been used up in making qualitative tests for gold, but, in default of more water, the chlorine-water solutions and precipitates yielded by the stannous chloride from each batch of tests were mixed together and evaporated to dryness and then scorified and cupelled so as to determine the amount of gold. The assays were not done separately on each test, as it was thought that the gold beads, if any, would be too small to weigh.

Southern Sea-waters.—The first batch of tests, Nos. 1 to 6, *i.e.*, the extracts from six litres, gave 0.003 grain of gold, *i.e.*, 0.508 grain of gold per ton, or 0.38 grain per cubic yard, or 0.032 m.grm. per litre.

Second Batch.—The precipitate from twelve litres used for the second set of tests gave 0.009 grain, *i.e.*, 0.76 grain of gold per ton, or 0.57 grain per cubic yard, or 0.048 m.grm. per litre. The film was treated twice with chlorine water, and the two extracts added together.

Third Batch.—9.025 litres gave 0.0069 grain of gold, *i.e.*, 1.09 grain per ton, or 0.58 grain per cubic yard, or 0.049 m.grm. per litre.

Northern Sea-waters.

8.100 litres gave 0.0060 grain of gold, equal to 0.75 grain per ton, or 0.56 grain per cubic yard, or 0.048 m.grm. per litre.

In calculating the amount of gold per ton or cubic yard, the specific gravity was in each case corrected to 1.026, *i.e.*, the mean results obtained by the *Challenger* Expedition, corrected to 15.5° C. for sea-water off the coast of New South Wales.

Before proceeding with further determinations of gold in sea-water, experiments were made to ascertain what loss of gold was sustained in the case of solutions containing known quantities of gold.

Experiments with Distilled Water and Added Gold.

The following experiments were made to ascertain whether small quantities of gold in dilute solution could be recovered by treatment with ferrous sulphate and other reagents. After adding the ferrous sulphate the solution was exposed in large new shallow photographer's developing dishes for some days, so that the ferrous sulphate might be slowly oxidised and precipitated; in some

* Read before the Royal Society of N. S. Wales.

cases glass cylinders were used and air blown through the solution. To complete the precipitation ammonia was added, the precipitate collected, washed, dried, scorified, and cupelled.

From the following results it will be seen that there was but little loss in some cases, but a good deal in others, partly due to imperfect precipitation by the ferrous sulphate, and partly to the loss during cupellation. In most cases the treatment with ferrous sulphate, oxidation and precipitation, was repeated upon the filtrate from the first precipitate.

1000 c.c. distilled water and 1 c.c. of 0.01 per cent AuCl_3 solution = 0.00154 grain gold.

1. Treated with 0.5 gm. FeSO_4 and NH_3
yielded 0.0015 gr.
2. Filtrate treated with 0.25 gm. FeSO_4
and NH_3 yielded 0.0000

Gold = 0.0015 "

1000 c.c. distilled water (containing 30 grms. NaCl) and 1 c.c. of 0.01 per cent AuCl_3 solution = 0.0015 grain of gold.

1. Treated with 0.5 gm. FeSO_4 and NH_3
yielded 0.0011 gr.
2. Filtrate treated with 0.25 gm. FeSO_4
and NH_3 yielded 0.0000

Gold = 0.0011 "

I.e., a loss of 0.0004 grain of gold or 26.6 per cent. The presence of the NaCl seems to increase the loss of gold.

1000 c.c. distilled water and 100 c.c. of 0.01 per cent AuCl_3 solution = 0.1543 grain gold.

1. Treated with 1 gm. FeSO_4 and NH_3
yielded 0.1253 gr.
 2. Filtrate treated with 0.5 gm. FeSO_4
and NH_3 yielded 0.0010 "
- 0.1263 "

I.e., a loss of 0.0280 grain gold or 18.14 per cent.

1000 c.c. distilled water and 100 c.c. of 0.01 per cent AuCl_3 solution = 0.1543 grain gold.

1. Treated with 1 gm. FeSO_4 and NH_3
yielded 0.1327 gr.
 2. Filtrate treated with 0.5 gm. FeSO_4
and NH_3 yielded 0.0010 "
- 0.1337 "

I.e., a loss of 0.0206 grain gold or 13.35 per cent.

Experiments with Sea-water and Added Gold.

1000 c.c. Coogee sea-water and 100 c.c. of 0.01 per cent AuCl_3 solution = 0.1543 grain of added gold.

1. Treated with 0.5 gm. FeSO_4 and NH_3
yielded 0.1430 gr.
 2. Filtrate treated with 0.25 gm. FeSO_4
and NH_3 yielded 0.0020 "
- 0.1450 "

I.e., a loss of 0.0093 grain of gold or 6.027 per cent.

1000 c.c. Coogee sea-water and 100 c.c. of 0.01 per cent AuCl_3 solution = 0.1543 grain gold.

1. Treated with 0.5 gm. FeSO_4 and NH_3
yielded 0.1415 gr.
 2. Filtrate treated with 0.25 gm. FeSO_4
and NH_3 yielded 0.0020 "
- 0.1435 "

I.e., a loss of 0.0108 grain gold or 7 per cent.

500 c.c. Coogee sea-water and 10 c.c. of 0.01 per cent AuCl_3 solution = 0.0154 grain gold.

1. Treated with 1 gm. FeSO_4 and NH_3
yielded 0.0095 gr.
 2. Filtrate treated with 0.5 gm. FeSO_4
and NH_3 yielded 0.0000
- 0.0095 "

I.e., a loss of 0.0059 grain gold or 38.31 per cent.

500 c.c. Coogee sea-water and 10 c.c. of 0.01 per cent AuCl_3 solution = 0.0154 grain gold.

1. Treated with barium chloride yielded 0.0013 gr.
 2. Filtrate treated with 1 gm. FeSO_4
and NH_3 yielded 0.0069 "
- 0.0082 "

I.e., a loss of 0.0072 grain gold or 46.75 per cent.

2000 c.c. Coogee sea-water and 50 c.c. of 0.01 per cent AuCl_3 solution = 0.0771 grain gold.

1. Treated with 1 gm. lead acetate in
acetic acid and precipitated by
sheet zinc yielded 0.0708 gr.
 2. Filtrate treated with 1 gm. FeSO_4
and NH_3 yielded 0.0000
- 0.0708 "

I.e., a loss of 0.0063 grain gold or 8.17 per cent.

2000 c.c. Jervis Bay sea-water and 25 c.c. of 0.01 per cent AuCl_3 solution = 0.0385 grain gold.

1. Treated with 1 gm. lead acetate and
precipitated by sheet zinc yielded 0.0235 gr.
 2. Filtrate treated with 1 gm. FeSO_4
and NH_3 yielded 0.0016 "
- 0.0251 "

I.e., a loss of 0.0134 grain gold or 34.8 per cent.

It must be borne in mind that to the loss of gold sustained in the above experiments should be added the amount of gold also present in the sea-water. The smallest loss seems to be sustained when the gold is precipitated by ferrous sulphate and ammonia, but even that process is far from satisfactory.

Additional Determinations of Gold in Sea-water from Coogee.

2000 c.c. treated with 0.5 gm. FeSO_4 and NH_3 yielded 0.0015 gr. = 0.76 grain per ton.

1. 9000 c.c. treated with 2.5
grms. of FeSO_4 , air
blown through and
 NH_3 added, yielded .. 0.0028 gr. = 0.31 gr. per ton.
 2. Filtrate treated with 1
gm. FeSO_4 and NH_3
added yielded 0.0035 gr. = 0.39 " "
- Total .. 0.0063 gr. = 0.70 " "

1. 2000 c.c. treated with 1
gm. lead acetate and
precipitated by sheet
zinc yielded 0.0003 gr. = 0.152 gr. per ton.
 2. Filtrate treated with 1
gm. FeSO_4 and NH_3
yielded 0.0002 gr. = 0.101 " "
- Total .. 0.0005 gr. = 0.253 " "

It was found when large quantities of Coogee sea-water *e.g.*, 45 litres, were treated with from 1.5 to 5 grms. of ferrous sulphate, followed by exposure for oxidation, scorification, and cupellation, that the amount of gold

obtained was very much less in proportion than that yielded by treating one or two litres.

Several trials were made, a larger quantity of ferrous sulphate would doubtless have given results similar to those obtained from two litres; but I have not had time to repeat the experiments with large quantities of ferrous sulphate—as dealing with large quantities is slow and laborious with ordinary laboratory appliances.

The inside of the 36-gallon cask which had contained the Coogee sea-water was scraped, but very imperfectly, about two ounces of scrapings obtained; they were incinerated, scorified, and cupelled, when a bead was obtained containing—

0.0070 grain of silver = 5 dwt. 5.43 gr. per ton.
0.0017 „ gold = 1 „ 6.46 „

Only a part of the barrel was scraped, and that not deeply; but the above results are quite sufficient to show that the gold and silver in sea-water are precipitated by the wood, &c.; hence water which has been kept in wooden vessels does not yield the full amount of these metals, and the very small amount of silver found in sea-water by Malaguti may have been due to his keeping the sea-water in a wooden cistern.

All my experiments were made upon sea-water collected and kept in glass vessels, with the exception of the later ones on Coogee water, which had been kept in the barrel.

Gold in Sea-water Collected off Jervis Bay.

1. 2000 c.c. treated with 1 grm. FeSO_4 yielded..	0.0001 gr. = 0.05 gr. per ton.
2. Filtrate treated with 0.5 grm. FeSO_4 and NH_3 yielded	0.0002 gr. = 0.101 „ „
Total.. ..	0.0003 0.151 „ „

1. 2000 c.c. treated with 1 grm. lead acetate and precipitated by sheet zinc yielded	0.0020 gr. = 1.016 gr. per ton.
2. Filtrate treated with 1 grm. FeSO_4 and NH_3 yielded	0.0000 gr. = 0.000 „ „
Total.. ..	0.0020 1.016 „ „

1000 c.c. treated with chlorine, and then with 5 c.c. carbon disulphide, to dissolve out any iodine or bromine which might have been set free, decanted, 1 grm. lead acetate added, and precipitated by zinc, yielded 0.0005 gr. = 0.508 gr. per ton.

1000 c.c. treated with 2 grms. of mercuric chloride for four days and then precipitated by H_2S , yielded 0.508 gr. gold per ton.

Experiments with other processes are now being carried out; but as they are not complete the results are deferred for a later paper.

To test the ordinary Sydney water supply, collected over a sandstone area, 124 lbs. weight of the laboratory tap-water was tested for silver and gold by adding 100 c.c. sulphurous acid, 5 grms. ferrous sulphate, and allowing to oxidise for several days; the iron hydroxide was then precipitated by ammonia, scorified, and cupelled, but neither gold nor silver was found.

The amount of gold obtained from sea-waters in the foregoing experiments must necessarily be less than the total amount of gold present in the water, since it was found that known quantities of gold chloride solution added to distilled and sea-waters and then estimated by precipitation, scorification, and cupellation nearly always showed a loss, and sometimes a very considerable one.

All the above evidence is in favour of gold being present in sea-water off the New South Wales coast in the proportion of about 0.5 to 1 grain per ton, or in round numbers from 130 to 260 tons of gold per cubic mile. This, of course, means an enormous amount for

the whole of the ocean, the cubic contents of which used to be put down at 400,000,000 cubic miles; and if the gold be uniformly present at the rate of 1 grain per ton the total amount would be over 100,000,000,000 tons of gold; a later estimate is 308,710,679 cubic miles, this even would mean over 75,000,000,000 tons of gold. But at the present day it would probably not pay to extract the gold by itself, although it might as a by-product in the manufacture of salt, bromine, &c. The enormous amount of gold in the sea is, however, probably very small in comparison with the amount scattered through sedimentary and crystallised rocks, *i.e.*, apart from gold in veins and other deposits.

Silver in Sea-water.

All the sea-waters gave some silver, usually from 1 to 2 grains per ton, but I consider the scorification and cupellation process lacking in the necessary precision for the exact determination of silver in such minute quantities as it exists in sea-water; I have therefore omitted all the determinations of silver from this paper, but I may publish them later on with the results of other experiments now in hand.

Malaguti estimated the amount of silver in sea-water at 0.001 grm. per 100 kilos. of sea-water, or at only 0.15 grains per ton; but I have quoted him more fully in a paper entitled "On the Removal of Gold and Silver from Sea-water by Muntz Metal Sheathing," which will appear in an early issue of this journal.

ON THE FORM OF THE ATOMS,

By C. FOURLINNIE.

WE have here a notice of a remarkable work extracted from the *Bulletin de la Société Chimique de Paris*.

The author endeavours to solve the following problem:—Can we explain the properties of the simple substances by admitting that their atoms are constituted of a unique and homogeneous substance having forms differing geometrically in each elementary body?

Limiting this research to the non-metals, the author reaches the conclusion that the non-metals arranged by Dumas in the same family possess atoms of the same form but of different dimensions, whilst the non-metals belonging to two different families have dissimilar atoms.

On carrying this analogy further, M. Fourlinnie shows that these atomic forms must be regular polyhedra; a conclusion perfectly in harmony with the fact that there can exist only five regular polyhedra corresponding to the five families of Dumas.

In order to effect this determination he has been led to compare the volumes of the different regular polyhedra, and he finds that the volumes of the hexahedron, the octahedron, the dodecahedron, and the icosahedron, inscribed in the same sphere, are relatively as the numbers 19, 16, 14, and 12, which are relatively the atomic weights of fluorine, oxygen, nitrogen, and carbon.

The author is then naturally led to conclude that the elements of the fluorine group have hexahedric atoms; those of the oxygen group, octahedric atoms; those of the nitrogen group, dodecahedric atoms; and those, lastly, of the carbon family, atoms having the form of regular icosahedra; whence, by exclusion, the regular tetrahedron belongs to hydrogen.

It further results that the simple bodies, the heads of the series F, O, N, C, have atoms possessing very distinctly the same apotheme, a circumstance which leads to the hope that we may, in accordance with the predictions of Schützenberger, fix the decimal divisions of the atomic weights by mathematical calculation.

After some interesting reflections on the attractive and repulsive actions of atoms, the author examines the consequence of his theory as regards atomicity and the combination of atoms among themselves.

When the atoms combine they take a state of stable equilibrium, where the axes—determined either by the surfaces (apothemes) or by the apices—coincide with each other.

By the aid of these considerations the double atomicity of oxygen is easily explained. It is the same with the triple atomicity of nitrogen; further, for this element the co-existence of the atomicities 3 and 5 meets with a striking appreciation. In the former case the equilibrium is determined by the apothemes, in the second by the apices.

For carbon the tetratomicity is more difficult; it necessitates an equilibrium, in part following the apothemes, and in part following the axes of the apices.

The ingenious theories of M. Fourlinnie are certainly not out of the reach of criticism. They recommend themselves to the favourable notice of the scientific world by their novelty and their originality.

They ought to be regarded as the germ of a new theory which may perhaps some day cast a novel light on the question of the mutual relations of the atomic weights.

It is, we believe, the first time that there has been given a relation of a mathematical order between the numerical values and the atomic weights of the elementary bodies fluorine, oxygen, nitrogen, carbon.

NOTE ON THE SOLUBILITY OF BISMUTH SULPHIDE IN SODIUM SULPHIDE, WITH SPECIAL REFERENCE TO THE ESTIMATION OF SMALL AMOUNTS OF BISMUTH IN ANTI-FRICTION ALLOYS.

By THOMAS B. STILLMAN.

THE method of separation of lead, copper, and bismuth from antimony, arsenic, and tin, by the use of sodium sulphide, is quite general. This is dependent upon the usually accepted statement that the sulphides of bismuth, lead, and copper are insoluble, and the sulphides of arsenic, antimony, and tin are soluble in sodium sulphide. This process of separation is employed in the analysis of various alloys, especially of anti-friction alloys, containing lead, tin, antimony, &c.

An alloy used for similar purposes, but containing, in addition to lead, copper, antimony, and tin, a very small amount of bismuth, was recently submitted to me for analysis.

After complete solution of the alloy in hydrochloric acid with a few drops of nitric acid, the acid was neutralised with sodium hydroxide, sodium sulphide solution (1·06 sp. gr.) added, and the heat applied for twenty minutes. The solution was filtered, and the filtrate examined for the antimony and tin with satisfactory results.

The precipitate of insoluble sulphides remaining upon the filter was found to contain lead and copper, but no bismuth. This indicated that the small amount of bismuth which was present in the alloy had gone into solution in the sodium sulphide.

To prove this theory, I weighed 0·128 gm. of pure bismuth nitrate, dissolved it in 25 c.c. of water with a few drops of nitric acid, the clear solution neutralised with sodium hydroxide, 75 c.c. solution of sodium sulphide added, and warmed to a temperature near boiling for twenty minutes. The solution was filtered from the bismuth sulphide, remaining insoluble in the sodium sulphide. The clear filtrate was rendered faintly acid with hydrochloric acid, when a brownish black precipitate immediately formed. This precipitate was filtered, dissolved in hot nitric acid and evaporated to dryness, and ignited in a weighed porcelain crucible. The residue obtained was 0·031 gm. of bismuth trioxide, and strongly yellow in colour. It was dissolved in a few drops of

hydrochloric acid, and the three following confirmatory tests for bismuth were made:—

1. A portion of the solution was poured into a large amount of water, forming immediately a white precipitate of bismuth oxychloride.

2. A portion was tested by Schneider's test, the most delicate test for bismuth, the reaction obtained being strong and characteristic.

3. A portion was diluted with water, not enough to cause precipitation, and the solution saturated with hydrogen sulphide. The precipitate formed was brownish-black in colour.

These three tests are absolutely confirmative of the presence of bismuth, and also show the absence of the other metals. By thus using pure bismuth nitrate for this test, lead, copper, antimony, and tin are not present.

If now an analyst should weigh 12 grms. of an alloy, composed approximately of lead 80 per cent, antimony 15 per cent, tin 4·75 per cent, and bismuth 0·25 per cent ("magnolia metal"), and sodium sulphide solution be used for the separation of the tin and antimony from the lead and bismuth, all of the bismuth present would pass into solution and escape determination by the analyst.

No analyst, however, would use as much as 12 grms. of such an alloy for analysis, but rather 1 or 2 grms.

If 1 gm. be taken and sodium sulphide used as above indicated, 3 per cent of bismuth might be present, and all of it pass into solution in the sodium sulphide instead of remaining as an insoluble sulphide with the lead sulphide. — *Journal of the American Chemical Society*, vol. xviii., No. 8, August, 1896.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY
SAMPLES OF THE WATER SUPPLIED TO LONDON
FOR THE MONTH ENDING AUGUST 31ST, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, September 12th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Aug. 1st to Aug. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined six were recorded as "clear but dull," the remainder being clear, bright, and well filtered.

We have again to record a deficiency of rainfall in the Thames Valley.

The average fall for the month is..	2·32 inches
The actual fall at Oxford has been ..	2·01 "
Deficiency ..	0·31 "

Making the total deficiency for this year 5·97 inches.

On the other hand the quality of the water is of very high standard, as the following bacteriological results show:—

	Colonies per c.c.
Thames water, unfiltered	1133
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	43
Ditto ditto lowest	6
Ditto ditto .. (12 samples) mean	17
New River water, unfiltered	361
New River water, from the Company's clear water well	3
River Lea water, unfiltered	537
River Lea water from the East London Com- pany's clear water well	5

The above results are confirmed by the chemical analysis.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

JAMES DEWAR.

THE INTRODUCTION OF STANDARD METHODS OF ANALYSIS.*

By the Baron HANNS JUPTNER VON JONSTORFF
(Neuberg, Austria).

(Concluded from p. 160).

As I also had frequently met with very considerable differences in the sulphur contents of the same sample of steel, I took from a cut piece of sheet iron, 30 millimetres broad and 6 millimetres thick, the high sulphur percentages of which permitted the weighing out of small samples, sixteen samples in the manner shown in Fig. 1, and with each two sulphur determinations were made so as to show that the differences were not due to the methods employed. The results were as follows:—

XIII. 0'058 0'048	IX. 0'053 0'060	V. 0'095 0'090	I. 0'092 0'092
XIV. 0'043 0'034	X. 0'058 0'062	VI. 0'070 0'074	II. 0'086 0'076
XV. 0'057 0'049	XI. 0'042 0'035	VII. 0'075 0'085	III. 0'095 0'098
XVI. 0'042 0'032	XII. 0'080 0'090	VIII. 0'075 0'088	IV. 0'053 0'053

The greatest difference between two pairs of determinations amounted to 0'013 per cent (sample viii.), and that at a place in which very varying sulphur contents adjoin each other (iii. with 0'097, iv. with 0'053, and xi. with 0'038 per cent of sulphur); whilst the maximum difference between all the sixteen mean analyses was 0'060.

The irregularity of the distribution is shown in Fig. 2.

In a large quantity of samples of filings irregularities in the composition of the material are exhibited by the differences in the analytical results. These are of so local a nature that they can only be detected under the microscope. The brittle parts of the material give finer filings than those which are more tough. The former must consequently collect at the bottom of the vessel that serves to receive the sample, more especially when it is violently stirred with the object of ensuring the best possible mixing.

A very interesting series of observations bearing on this point have been published by L. Schneider (*Oesterr. Zeit.*

für Berg- und Hüttenwesen, 1894, p. 244). The only source of regret is that the two portions of the material were not analysed separately. The results are given in the Table.

In sample No. 13, the laminated portion contained 1'0 per cent of chromium, and the powder contained 0'7 per cent. The comminution of steel samples is effected by means of hammering. In the figures given in Columns 3 and 4 in Nos. 16 and 17, there appears to be a misprint in the original, as the total exceeds 100.

The behaviour is the same with graphitic grey pig-iron, especially in metal average analyses. Thus, I found (*Oesterreichische Zeitschrift für Berg- und Hüttenwesen*, 1890, p. 273) in an average sample of spiegeleisen, in nine determinations, variations in the manganese contents between 6'3 and 13'3 per cent, an observation which was confirmed by J. Kail (*Ibid.*, p. 506) for other elements.

To avoid these difficulties, not only must the irregular distribution of the elements in iron and steel materials be closely studied, but also some agreement must be arrived at as to the method of taking the samples. In this last connection I would like to submit the two following proposals:—

(a). *That it is best entirely to Exclude Average Samples of Metals.*—In the majority of cases it is much better to examine a number of separate samples, and to calculate the average from these results. Not only in this way may a satisfactory agreement be arrived at between the various samples, but a good idea is also obtained of the variations in composition of the material under investigation.

(b). *In the case of grey or mottled pig-iron*, in the determination of carbon, only so much of the metal should be broken down as is necessary for the test; that is to say, the whole of the powdered material is to be used up in the determination.

It is scarcely necessary to point out that all solutions used should be thoroughly mixed, whether these are solutions of the samples or standard solutions.

The detailed consideration of the sources of error in chemical analyses will have shown, even to non-chemists, that chemical analysis, especially that of steel, is by no means a simple matter, and that it is necessary to place it in the hands of skilled chemists if it is a question of obtaining accurate results. Is, however, such a degree of accuracy always necessary? To answer this question, the various uses to which analysis is put must be considered. One must distinguish between (1) analyses which are intended for use in controlling the work at the works; (2) trade analyses; (3) analyses which are to show the reason why the material under examination possesses certain properties, or whether it is suitable for certain definite purposes; (4) analyses connected with scientific investigations, where it is a question of ascertaining the constitution of iron materials, and the investigation of the relations existing between their chemical composition and their physical properties, &c.

For the purposes of works control, relative accuracy is adequate; that is to say, the method must not only show a plus or minus of the substance to be determined, but also with equal contents give good agreement, at least in all cases which may occur in the locality in question. It is desirable that these results should agree as nearly as possible with the true percentages, but this is a secondary matter as compared with the necessity of making as many as possible of these determinations simultaneously, and in the shortest time.

Such a method, for instance, is the well-known Eggertz colorimetric method for the determination of carbon. This gives results which are quite adequate for work control purposes in all cases where the material of the sample is produced under similar conditions as to hardening. Under no circumstances, however, can it be adopted if it is a question of the simultaneous examination of unhardened, hardened, and annealed steel, or of foreign steels whose methods of manufacture are not exactly known.

* Read before the Iron and Steel Institute.

No.	Steel.	Laminated residue. Per cent.	Pulverulent residue. Per cent.	Percentage composition.									
				C.	Si.	P.	S.	Mn.	Cu.	W.	Cr.	Ni.	
1.	Nickel steel	99	1	0'42	0'22	—	—	0'22	—	—	—	6'0	
2.	Filings from a foreign steel sample	99	1	0'46	0'15	0'04	0'01	0'48	0'08	—	—	—	
3.	Krupp tool steel	98	2	0'90	0'28	0'02	0'01	0'26	0'05	0'11	—	—	
4.	St. Egyd steel	96	4	0'67	0'37	0'04	0'05	0'23	—	—	—	—	
5.	St. Egyd steel	92	8	1'20	0'35	0'02	0'03	0'23	—	—	—	—	
6.	Puddled steel	94	6	0'90	0'17	0'02	0'01	0'11	—	—	—	—	
7.	Witkowitz steel <i>a</i>	90	10	0'15	?	—	—	—	—	—	—	—	
8.	Witkowitz steel <i>b</i>	90	10	0'08	?	—	—	—	—	—	—	—	
9.	Chrome steel	90	10	?	—	—	—	—	—	—	0'95	—	
10.	Zeltweg steel	90	10	0'30	0'02	0'09	?	0'20	—	—	—	—	
11.	Neuberg steel	90	10	0'52	0'36	0'15	0'06	0'39	0'18	—	—	—	
12.	Open-hearth steel from Donawitz	89	11	0'20	0'04	0'08	?	0'13	—	—	—	—	
13.	Chrome steel	85	15	1'45	0'31	0'01	0'02	0'42	0'03	—	1'00	—	
14.	Neuberg steel	78	22	0'56	0'44	0'08	0'05	0'47	0'10	—	—	—	
15.	Riffle steel	78	22	1'24	0'81	0'02	0'02	0'21	—	1'90	—	—	
16.	Open-hearth steel <i>a</i>	69	32	0'13	0'02	0'08	0'04	0'47	0'03	—	—	—	
17.	Open-hearth steel <i>b</i>	68	40	0'14	0'02	0'07	0'03	0'17	0'01	—	—	—	
18.	Eibiswald puddled steel	66	34	0'90	0'08	0'02	0'02	0'13	—	—	—	—	
19.	Tungsten steel from Kapfenburg	60	40	2'07	0'70	0'03	0'01	0'54	0'01	6'13	—	—	
20.	Böhler tool steel.. .. .	50	50	1'20	0'20	0'03	0'02	0'12	—	—	—	—	
21.	Crucible steel	32	68	0'83	0'08	0'03	0'02	0'31	0'04	—	2'50	—	
22.	Neuberg tungsten steel	5	95	2'60	0'34	?	0'01	?	0'01	6'40	0'10	—	
23.	Musket steel.. .. .	0	100	2'24	0'99	0'04	0'02	1'56	tr.	6'26	0'22	—	

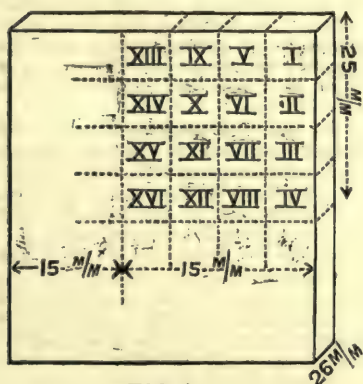


FIG. 1.

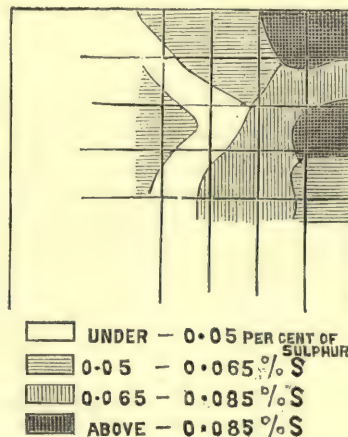


FIG 2

A second example is the phosphorus determination by the molybdate method by the aid of the rotation apparatus. It gives results which are perfectly satisfactory if all conditions as to its use are *exactly* complied with, and the point taken into consideration that the calculation factor varies with the volume of the precipitate. It follows that this method can be well recommended not only for works control purposes, but generally. Yet by slight variations in the manipulation the method gives differences which are so great that it can only be entrusted to trustworthy hands, even if it is only a question of works control analyses.

In the case of commercial analyses, to which also those analyses belong that are intended to ensure that the percentage limits of chemical composition required by contract are maintained, it is only possible to be content with this kind of requirement when both parties, the buyers and the sellers, have agreed to some method for the determination of each particular substance. Under certain conditions, therefore, it is possible to rest satisfied with *relative accuracy* even in trade analyses; but, as a general rule, it is best to aim at the highest possible degree of accuracy.

The question is quite different in the instances given under (3) and (4). Here the requirement of endeavouring

to attain a maximum degree of accuracy takes the foremost place, while the possibility of making many determinations rapidly and at the same time is not so important.

It is therefore necessary to distinguish between—(a). *Methods for works control*, and, under certain circumstances, for trade purposes; and (b). *Methods for all other purposes*. With regard to these latter, I should like to draw attention to one other circumstance. Modern methods of analysis, such as are actually employed daily in practice, are, with almost the single exception of the determination of graphite, complete analyses. Iron materials are, however, in no way homogeneous substances such as minerals, but are mixtures of various compounds, analogous, that is, to rocks composed of several minerals, and there can be no question but that many samples of iron of quite identical elementary composition, according to the kind and quality of their inner components, may show altogether different physical properties. It has so far only been attempted to explain this in a few cases. At the present time the different forms of carbon are more intimately known, but practical methods for their determination suitable for use in the technical laboratories are wanting. With reference to certain other elements, phosphorus (L. Schneider, *Oesterreichische Zeitschrift für*

Berg- und Hüttenwesen, 1886, p. 736; H. von Jüptner, *Ibid.*, 1894, p. 209), chromium (H. Behrens and Van Linge, *Fresenius's Zeitschrift*, xxxiii., p. 573; H. von Jüptner, *Oesterr. Zeit. f. Berg- und Hüttenwesen*, 1896, No. 2), tungsten (L. Schneider, *Oesterr. Zeit.*, 1895, No. 18), and others, some information has been given, but the notes referred to are very isolated in character, and consequently require confirmation by numerous investigations before general conclusions can be drawn from them. We know that all elements which can be precipitated by sulphuretted hydrogen are completely contained in the residue insoluble in dilute sulphuric acid (F. G. Müller, *Stahl und Eisen*, 1888, p. 293; Reinhardt, *Ibid.*, 1889, p. 405; von Reis, *Ibid.*, 1889, p. 720); that copper separates out in the iron mass in the form of metallic shots or as sulphide; that phosphorus is partly evolved in the form of phosphuretted hydrogen by dilute acids, but that it in part remains undissolved (H. von Jüptner, *Oesterr. Zeit. f. Berg- und Hüttenwesen*, 1894, p. 208) as iron phosphide or manganese phosphide, Fe_3P or Mn_3P_2 ; that slag is included in the metal, &c., &c.

It is just these kinds of investigations, however, which are of especial value, not only from a scientific point of view, but to an eminent degree for technical practice; for it is only when a more accurate knowledge is obtained of the inner constitution of the varieties of iron met with in practice—and methods are known by which in every case this may be readily and accurately determined—that it will be possible to choose for every purpose a material of proper chemical composition and mechanical treatment, and to find means and ways in order to prepare it with certainty for every case. In this connection not only must chemical examination be adopted, but microscopic as well, a method which so far does not receive nearly the amount of attention it deserves.

In view of what has just been discussed, the questions to be considered—as I showed at the recent International Conference for the Unification of Testing Methods at Zürich—may in their general scope be briefly sketched out as follows:—There require to be studied—(1) The irregular character of the samples, and some agreement as to the method of taking the samples, must be arrived at, both as regards these irregularities and also any impurities introduced in the course of their being broken down to size. (2) At least all the more important methods of determination for all the constituents met with in iron and steel materials, including slag and gas inclusions, should be thoroughly studied and compared with one another, taking into consideration all possible sources of error. We can then either rest satisfied with this comparison or pass to the setting up of standard methods. In any case, it will be necessary to distinguish between methods for the works control, &c., in which, in the first instance, rapidity of completion has to be considered, and which may be defined as works assays, and the analytical methods required for every other purpose in which accuracy is the main requirement. (3) We must not confine ourselves to determinations of the various elements, but must direct our attention to such matters as permit of the various forms and combinations in which the several constituents can occur in technical varieties of iron, being distinguished and quantitatively determined.

In view of all that has been said above, it follows that the scope of the necessary inquiry is of an extremely wide character. It is so wide indeed that it is scarcely desirable to attempt the solution at the same time of all the questions requiring consideration. It would be better perhaps, to endeavour to solve these one after the other, and to rest contented at first with the following:—(1) Investigations relating to the want of homogeneity in the samples, and to some decision as to the method of sampling; (2) examining the methods for the determination of the main constituents—that is to say, of carbon, silicon, manganese, sulphur, phosphorus, copper, and slag. (3) Since, moreover, as has been pointed out, the value of the atomic weights on which the analytical cal-

culations are based have at least in certain cases considerable influence on the results, it is desirable to arrive at either an agreement, perhaps temporary in character, as to the values to be adopted, or else to revise the atomic weights necessary in connection with the methods under examination.

To arrive at a general agreement of the methods to be examined, it would appear desirable, from the very commencement, to lay down definitely the general principles which are to be adopted. Much that has to do with this has been already shown, so that I may confine myself to a few brief remarks on this point.

It must not be forgotten that we have to consider in the first instance, practical work, and that even for our scientific purposes, which we also wish to place at the service of practical work, very tedious or troublesome methods have no value, or at most but very little. In this case, too, it is usually not so much the question of a single analysis, as of analytical material wide in scope that has to be the basis for further study.

But even for theoretical purposes, other conditions being equal, simple methods appear more desirable than more complicated ones, for every operation introduces sources of error; the greater the number of operations necessary and the longer these take, the greater both in number and in degree are the errors to which the analyst is exposed.

Permit me to give an example. The following method for the determination of phosphorus was proposed:—The phosphorus is to be precipitated from a nitric acid solution as ammonium phosphomolybdate, the precipitate collected on a filter, dissolved, precipitated with magnesia mixture, filtered, again dissolved, and finally titrated with uranium acetate. Why was not the phosphomolybdate, or at least the magnesia precipitate, weighed direct?

That we have to distinguish between works assays and precise analytical methods has been already pointed out. It is naturally advantageous, however, for a method to possess at the same time both the valuable properties of assay methods and of scientific methods, and consequently to be suited to both purposes.

It must not be forgotten that skill, personal factors, exceptional or other circumstances, may cause one analyst to prefer one method and another a second. This is a circumstance which it seems to me should be considered, to reduce personal errors to a minimum, and I should therefore consider it desirable that for every element many methods, based on as widely differing facts as possible, should be tested, and both their relative and their absolute accuracy ascertained.

It may here be pointed out that it can be by no means our aim to arrange normal methods, which are to be used always, under all conditions, and at all times. On the contrary, it must be left to every chemist to work as he thinks best, and the progress which scientific knowledge is making must also be taken into consideration—a progress that now-a-days is enormous. On the other hand, as has been pointed out, our aim must be to arrange for as many different methods as possible, and to ascertain their relative conditions of value. These methods are to serve as standard methods in investigating the particular method used by any individual analyst, or new methods, and are always to be used when differences in the results of analyses made at different laboratories have to be explained. But to be in accord with scientific progress, any other methods which may from time to time be proposed must be all included in the scope of the investigations.

Sources of Error in Alkalimetry.—Fr. Scheiding (*Zeit. f. Angewandte Chemie*).—The author lays especial weight on the influence of carbonic acid. He considers it fallacious to allow lye to stand for hours in an open bottle and then afterwards execute titrations in the cold, using phenolphthalein as indicator.

NOTICES OF BOOKS.

A Systematic Handbook of Volumetric Analysis; or, the Quantitative Estimation of Chemical Substances by Measure applied to Liquids, Solids, and Gases. Adapted to the requirements of Pure Chemical Research, Pathological Chemistry, Pharmacy, Metallurgy, Manufacturing Chemistry, Photography, &c., and for the Calculation of Substances used in Commerce, Agriculture, and the Arts. By FRANCIS SUTTON, F.I.C., F.C.S., Public Analyst for the County of Norfolk. Seventh Edition, Enlarged and Improved. London: J. and A. Churchill. 1896. Pp. 587.

"SUTTON'S Volumetric Analysis" has been for more than thirty years an indispensable laboratory companion, and has been regularly enlarged and improved in accordance with the extension of volumetric methods. This will be at once seen on comparing the first edition with the work as it now appears. In the earlier editions gas-analysis was overlooked—being, in fact, almost unknown. The analysis of water consisted simply of the Clarke method for the determination of its hardness, the estimation of nitrogen not being attempted either by the Frankland, the Wanklyn, or the Kjeldahl methods, which were in those days non-existent. We now find a microscopic examination recommended, not in the place of chemical analysis, but as a useful adjunct. The biological procedures are scarcely noticed. The Frankland and Armstrong method receives a more extended notice than in some of the earlier editions; and, on the other hand, less space is devoted to the Wanklyn and Chapman application of the Nessler reaction. The determination of the oxygen existing in solution in waters is duly noticed as regards its application to polluted waters. It will be remarked, however, that the names of Wanklyn, Dewar, and Tidy do not occur in the index.

The chapter on indicators is very valuable, and includes the latest observations, such as those of Mylius and Förster.

We are correctly informed that in gas-analysis the apparatus of Scheibler is practically superseded.

We cannot congratulate the author on having retained the term "indigo-carmin," a solecism as painful as that of the modern draper and modiste when they call a bluish grey shade "gobelin."

Full instructions are given for the detection of phosphoric acid in water.

A paragraph is given on reporting the results of water analysis—the joint opinion of special committees of the British and the American Associations. The report is to be found in full in the CHEMICAL NEWS (vol. lx., pp. 203, 204).

Without any further examination, we may safely say that it is a book with which every laboratory ought to be furnished.

Elementary Quantitative Chemical Analysis. Adapted for Use in the Laboratories of Colleges and Schools. By FRANK CLOWES, D.Sc., F.I.C., Professor of Chemistry in the University College, Nottingham, and J. BERNARD COLEMAN, A.R.C.Sc., F.I.C., Professor of Chemistry in the South-West London Polytechnic. London: J. and A. Churchill. 1896. Pp. 238.

THIS book is divided into sections, treating successively of general processes, gravimetric analysis, volumetric analysis, of the analysis of complex substances, of gas-analysis, and including tables of reference.

The various processes will be found to be carefully and clearly described, and may be followed with confidence. Among the complex substances examined we find no mention of water further than the determination of its "hardness."

The apparatus described for the volumetric determination of gases are those of Hempel and Lunge.

Among the typical results of analysis we find the composition of Nottingham coal-gas. It appears to be absolutely free from carbonic acid and from sulphur compounds, but is contaminated with 6.6 per cent carbon monoxide.

In the table of the elements argon and helium are absent, glucinum figures under the name beryllium, and didymium is retained in preference to its components neodymium and praseodymium.

The Book of the Dairy: a Manual of the Science and Practice of Dairy Work. Translated from the German of W. FLEISCHMANN, Ph.D., Professor of Agriculture, and Director of the Agricultural Institute, Königsberg University, Prussia, Honorary Member of the Royal Agricultural Society of England. By C. M. AIKMAN, M.A., Sc.D., F.R.S.E., F.I.C., and R. P. WRIGHT, F.H.A.S., F.R.S. Edin. London, Glasgow, and Dublin: Blackie and Son, Lim. 1896. 8vo., pp. 344.

Two facts cited in the translator's preface show that the British dairyman requires further instruction in his business. An income of £32,000,000 is derived from the sale of dairy produce at home, or one-sixth of the whole income of British agriculture. Yet we import from the Continent butter and cheese to the annual value of more than £20,000,000. Hence we have still vast room for improvement! This must especially be admitted if it is considered that our climate is admirably adapted for grazing purposes, whilst land fit for pasturage is lying waste and idle. Hence one of the most important remedies for the present agricultural depression is the diffusion of practical knowledge on the production of butter and cheese, and its general adoption. According to the author, and according to actual facts, we have in this country most to learn from Swiss practice; little, if anything, to learn from Belgium, as the odour of Limburg cheese has long been a standing joke. It is not gratifying to learn that the Dutch "Edam" cheese is largely exported to Australia. Some Dutch cheeses, like those of Suffolk, are almost hard enough for use as projectiles.

From German practice little is to be learnt on the preparation of cheese and butter. But Prof. Fleischmann has carefully studied and collated the methods of the countries and the special districts where dairying is carried on most successfully, comparing the procedures employed with the produce obtained, and is thus successful in giving most valuable advice to the dairyman.

As in all other works on the composition of milk, we have found nothing either to confirm or to refute the empirical notion that the milk of short-horn cows is decidedly poorer than that of the long-horn's of Lancashire and the West Riding. Dr. Vieth's analysis, here quoted, shows that the milk of short-horns is poorer than that of the Jersey breed, though not to the traditional extent.

The employment of milch-cows as beasts of draught or burden is rightly condemned, but it is not common in Britain. The author's strictures on dishorning cattle are not endorsed by the translators, who contend—in our opinion with justice—that it is really humane to the cattle, and removes a source of danger to the attendants. We may here remark that in countries free from wolves, &c., pugnacious bulls should not be used for breeding.

The illustrations with which the book is enriched are very appropriate.

We remark with regret that although Ireland is naturally better adapted for dairying industries than England or Scotland, yet Irish cheese does not figure in the market, and that Irish butters are being more and more displaced by Continental produce. Why is this?

CORRESPONDENCE.

THE SCIENCE AND ART DEPARTMENT.

To the Editor of the Chemical News.

SIR,—When some months ago it was rumoured that the Science and Art Department intended to modify their system of payments, and to abolish "payment on results," many of us rejoiced, and felt that at last there was some chance that the examination incubus which was smothering scientific teaching throughout the country would be removed. Alas! the regulations contained in the new edition of the "Science Directory" just published show that, so far from being relaxed, the cords of examinationism are to be drawn tighter than ever.

The payments under the new system are to take the form of attendance grants, at so much per head per attendance, the amount varying according to the efficiency of the teaching as measured by the report of the Inspector and the success of the class at the May examinations. No hint is given as to the relative importance which will be attached to the two factors. So it will be seen that there is still payment on results, though on a different and far less satisfactory—because less open—system.

Other regulations, now introduced for the first time, are very much worse, educationally, than any previously in force. Classes are to be in three stages (Elementary, Advanced, and Honours), but the new regulations as to payment apply only to the first two. These classes may not be taught together, and no student is to be admitted to an advanced class till he has passed the Science and Art Department Examination in the elementary stage.

These regulations destroy all trace of freedom in teaching. Hitherto a teacher has been to some extent free to teach on the lines he thought best, and to send his students up for examination, trusting to their being able to pass the examinations, and they were free to take either the elementary or advanced paper as they thought fit. This is no longer possible. No subject can be taught as a whole, but must be broken up into stages,—not according to any natural division of the subject or the judgment of the teacher, but according to the arbitrarily arranged syllabus of the Department, and the fitness of a student to pass from one stage to another is to be judged entirely by his success or failure in the Science and Art Department Examinations.

Under the old regulations good students often took the Advanced or sometimes even its Honours paper after one session of instruction in a class. Now that is not to be allowed. However well a student may be prepared, however much time he may give to study, however many hours per week may be given to teaching in the class, he will still have to go up for the Elementary Examination. This, I venture to say, the best students will not do.

In addition, there are regulations which will necessarily tend to the shortening of all lessons to the minimum of one hour for lectures, and one and a half hour—a ridiculously inadequate time—for laboratory instruction, and vexatious and troublesome rules as to the keeping of the class registers.

On the whole the new regulations are decidedly retrograde, and must still further lower the standard of teaching under the Department, and bring more discredit on to the whole system.

The way in which the changes have been made is also most unjust. The circular notifying them was sent out after many institutions had made and published their arrangements for the coming session, and the Directory containing the details has only just been issued after many classes have commenced work.

Surely for such serious changes ample notice should have been given.

The whole of the changes, in common with many of the existing regulations, seem based on the assumption

that teachers are ignorant, incompetent, and dishonest, and that knowledge of science and how it should be taught is only to be found in the officials at South Kensington.—I am, &c.,

S.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 10, September 7, 1896.

The inauguration of the statues erected to Pasteur, Florian, and the Abbé de Sauvages at Alais were arranged to take place on September 26th and 27th.

Discharge of Electrified Bodies by the X Rays.—Emilio Villari.—Will be inserted in full.

Emission of the X Rays.—Ch. E. Guillaume.—The law of emission as a function of the angle is not peculiar to the X rays; we arrive at analogous relations in the case of ordinary light whenever it emanates from a body sufficiently transparent. The law of the cosine ceases to be true whenever for the surface of emission there is substituted a volume of emission of finite thickness.

No. 11, September 14, 1896.

Simultaneous Presence of Laccase and of Tyrosinase in the Juice of certain Fungi.—G. Bertrand.—From one and the same juice extracted from certain fungi we may obtain on the one hand a liquid very rich in laccase, but without action on the tyrosin, and, on the other hand, a solution which scarcely shows the reactions of this soluble ferment, but possessing those of tyrosinase.

Revue Universelle des Mines et de la Metallurgie.

Series 3, Vol. xxxv., No. 1.

This number contains no chemical matter.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. i., No. 8.

Researches on the Structure of Metals, its Genesis, and its Transformations.—Prof. Roberts-Austen and F. Osmond.—This memoir is from English sources.

MISCELLANEOUS.

National Value of Chemistry.—It is fair to hold that the country that has the best chemists will, in the long run, be the most prosperous and the most powerful. It will have at the lowest cost the best food, the best manufactured materials, the fewest wastes and unutilised forms of matters, the best guns, the strongest explosives, the most resistant armour. Its inhabitants will make the best use of their country's resources; they will be the most healthy, the most free from disease; they will oppose the least resistance to favourable evolution; they will be the most thrifty and the least dependent on other nations. The education of its people in chemistry and the physical sciences is the most paying investment that a country can make. Competition to-day between nations is essentially a competition in the science and applications of chemistry.—*North American Review.*

TO CORRESPONDENTS.

H. L.—We can suggest no better or safer way than to sterilise the mixture by heat.

ERRATUM.—P. 76, col. 2, line 30 from bottom, for "o'19" read "o'019."

THE CHEMICAL NEWS.

Vol. LXXIV., No. 1924.

MEASUREMENT OF ELECTRIC CURRENTS THROUGH AIR AT DIFFERENT DENSITIES DOWN TO ONE FIVE-MILLIONTH OF THE DENSITY OF ORDINARY AIR.*

By Lord KELVIN, J. T. BOTTOMLEY, and
MAGNUS MACLEAN.

THE apparatus used in these experiments consisted of—(1) A cylindrical tube 13 c.m. long and $1\frac{1}{4}$ c.m. diameter, with two aluminium wires as terminals ground to points 1·5 c.m. apart; (2) a large Wimshurst electrostatic machine of 24 plates; (3) a high-resistance mirror galvanometer to measure the current between the aluminium-point terminals inside the tube; (4) an electrostatic voltmeter to measure the difference of potential between the terminals of the tube; (5) a five-fall Sprengel pump, by means of which the density of the air inside the tube could be reduced to any desired extent. The galvanometer was placed on a block of paraffin between one terminal of the electric machine and one terminal of the glass tube. Its deflections were read by a telescope and its sensibility was arranged by external magnets, so that one division of deflection corresponded to 0·3 mikroampère. Our method of experimenting was to keep the density of the air constant while we varied the difference of potential between the terminals of the tube, and taking simultaneous readings on the voltmeter and on the galvanometer. The electric potential was varied either by varying the speed of rotation of the machine or by varying the distance between the needle-point terminals of the machine, or by a combination of both.

We found that at ordinary atmospheric density it requires a difference of potential of between 2000 and 3000 volts at the terminals of the tube before the galvanometer indicates any current. As the difference of potential is now increased, the current through the galvanometer increases at a greater ratio, so that if a curve be drawn with differences of potential as abscissæ and galvanometer readings or currents as ordinates, the curve is always concave towards the axis of current. Through this particular tube the currents at 3000, 5000, and 8000 volts difference of potential were 7·2, 17·6, and 63·2 mikroampère respectively. As the density of the air was diminished, the difference of potential necessary to start a current, as indicated by the galvanometer, gradually diminished also, till, at a density of about $\frac{1}{1000000}$ of the ordinary density, a few score volts were sufficient to start a current. For the same difference of potential the current increased as the density of the air diminished; or otherwise, the same current was obtained by smaller differences of potential as the density of the air was reduced. Thus a current of about 50 mikroampère was obtained by differences of potential of 7400, 1090, 700, 370, 405, 570 volts, when the densities of the air were 1 (ordinary density), 0·058, 0·0093, 0·0007, 0·00006, 0·000024 respectively; or otherwise, when the air pressures were 750, 44, 7, $\frac{1}{2}$, $\frac{1}{10}$, $\frac{1}{25}$, m.m. of mercury respectively.

As the air density was still further reduced, the difference of potential necessary to start a current increased, and the current for the same difference of potential diminished. Thus, when the density of the air was reduced to one five-millionth of the density of air at ordinary atmospheric pressure and temperature, differ-

ences of potential of 3000, 5000, and 8000 volts gave currents of 1·3, 4·4, and 14·6 mikroampère respectively.

If a curve be drawn for a constant difference of potential, with air densities as abscissæ and currents as ordinates, we find the curve rising as the air density is diminished to about $\frac{1}{1000000}$ or $\frac{1}{100000}$ of ordinary density; then falling again as the density is still further reduced to about a five-millionth of ordinary density. This is the lowest density we have experimented with, but we have no reason to doubt that at very much lower densities we would still be able to get measurable currents through the tube.

We are now experimenting with a tube 13 c.m. long and $1\frac{1}{4}$ c.m. diameter, having ball terminals of $\frac{1}{4}$ c.m. diameter and about 2 m.m. apart. The investigation is not complete enough for publishing any results.

CHEMICAL EDUCATION IN ENGLAND AND GERMANY.*

By Sir HENRY ROSCOE.

THE question as to how far the scientific, and especially the chemical, education in Germany is superior to that in England, and how far that superiority has influenced the German chemical industries as against our own, is one which at the present moment has come into prominence in the public prints. As the question of scientific education is one which the section has for some time past considered, it cannot be inappropriate at the present moment to introduce a discussion on this subject from a scientific point of view. That in Germany the appreciation of the national value of a high scientific education is greater than it is at the present day in England is a universally admitted fact. In that country we find Government institutions of every kind for the advancement of the highest scientific instruction in all branches; and Englishmen have not been slow to avail themselves of the generosity of the German nation in studying in that country under conditions and at a cost which their native land does not afford them. And the question, then, may well be asked, has the admitted want of this largely-developed higher scientific instruction in England been detrimental to the prosperity and progress of chemical industry in this country? And, on the other hand, has the existence of this facility in Germany fostered chemical manufactures and trades in that country? If this is so, as many believe, the point to enquire is in what way can we in England be placed in a position successfully to compete with Germany.

Although I am not one of those who take a pessimistic view of our national industries, chemical or otherwise, I have no doubt that many of the complaints which we hear are well founded.

In the opinion of some who have favoured the public with their views, the evil is to be found in the want of appreciation of science and of original research on the part of the manufacturers. If, say they, our manufacturers were as fully aware of the importance of the assistance which scientific investigation gives to their industries as are our German competitors, England would be well able to furnish educated men qualified for the work. Others, again, take a more general view, and see the origin of the difficulty in the system of university education, especially in our older seats of learning, where science teaching is not given free scope, and where too great a weight is laid on examination results, and little encouragement given to original scientific investigation. And those who take this view further insist that if science found its legitimate expression in the university curriculum and available honours, schools would not be slow to take up the matter

* Read before the British Association (Section A), Liverpool Meeting, 1896.

* Read before the British Association (Section B), Liverpool Meeting, 1896.

and to see that *their* instruction was made to lead up to university requirements, and thus the general scientific instruction in the country would be improved.

Both of these causes are probably at work in preventing that direct application of chemical research to industry, upon which alone its future success must depend. As an instance of this want of appreciation on the part of manufacturers and capitalists, I may remind the section that the initiation, from both its theoretical and practical side, of the great colour industry took place in this country. Not only was the first of these colours discovered by an Englishman, not only were all the raw materials required to be had in quantity in England—and nowhere else,—but the scientific men who have since been the means of inaugurating and carrying out in Germany this enormous industry were, at the inception of that industry, actually resident in Lancashire, and carried to Germany the practical results of their knowledge of English manufacturing methods, at that time scarcely known in their own country; and there is no reason in the nature of things why Caro, Martius, and Pauli, men who have since made their name illustrious in connection with German industries, should not, like our distinguished President of the Section, have remained in England to found here the industries which have brought millions into the revenues of Germany. What was it that prevented them? Simply the want of foresight and of scientific knowledge and zeal among the English chemical manufacturers and capitalists of that time. If these men had been able to obtain financial support in Lancashire some thirty or forty years ago, the colour manufacture would have been a Lancashire instead of a German industry. Have we improved matters since that date? Are our capitalists any more ready than they were to acknowledge the dependence of industry on science, and to take steps in advance in new directions? Are our chemical industries on the wane, and must we in all departments yield the palm to Germany. The interesting address of our president has proved that this is not the case, and the success which has attended his labours and that of the able men with whom he is surrounded in his work is a signal example of what can be done in this country in opening out new paths. Another instance of this kind, also mentioned by him, is one which points in the same direction. The matters to which I refer are new departures due mainly to the scientific and practical genius of my friend Mr. Castner. It is almost a startling fact that sodium, which a few years ago was a chemical rarity, is now made by Davy's original electrolytic process, to the amount of five tons per week in one single works; that sodium peroxide, a body scarcely ever seen, even in the chemical laboratory, is also manufactured by scores of tons. Moreover, that electricity, which is every day becoming more and more the handmaid of the chemist, so that instead of our wandering to Section A, we compel that section to come to us, electricity, I say, is now called into requisition to manufacture two of the most common articles—caustic soda and bleaching powder. In both of these instances no difficulty has been found in obtaining requisite financial support, and in these instances England has led the way. And not only does America follow the lead, but the great firm of Solvay, which has always been the first to encourage and develop new applications of science to industry, has accepted this English invention as being one full of promise for the future. These instances, then, serve to show in the first place that there are people in England capable of originating discoveries, and also persons who are willing to give the financial support for the foundation of industries dependent on those discoveries.

But more than this, I maintain that with the single exception of colour manufacture, English chemists and English capitalists have in the past taken the lead in every branch of chemical industry. Our President's Address proved this up to the hilt in the case of chlorine. From the hour when Davy, in 1810, gave the proof of the

true character of this gas, and even before that, up to the present day, the only names, with the exception of Berthollet and Le Blanc, mentioned in the address are those of Englishmen—Tennant, Gossage, Muspratt, Dunlop, Weldon, and Deacon—are the men who made the real permanent advances in the industry of chlorine. In the cognate branch of the soda industry Le Blanc certainly claims the first place. But it is to Englishmen that the lasting success of Le Blanc's process is due; for without Glover's towers, Shank's lixiviating vats, and Chance's sulphur recovery process—and I might mention many others—the application of the great Frenchman's discovery must long ago have died a natural death; and these, and these alone, keep it now alive. Nor must we forget that, whilst the success of the ammonia-soda process is greatly due to Solvay, not only was the reaction given by two Englishmen—Dyer and Hemming, in 1838,—but the working out of the details of the process was accomplished on English soil by our President, who, from his long residence amongst us, and from the great work which during that time he has accomplished, we may claim—and I trust he will not be displeased—to be our countryman.

In other more general respects English chemical industry is to the fore. Our Society of Chemical Industry, founded fifteen years ago in this district, is the largest and most active in the world, and our journal is acknowledged both at home and abroad to be the best in existence.

But though we may justly point with pride to the work which has been done, and which is still being done, in this country in establishing chemical industries, it must be admitted that much remains to be done if we are to keep pace with the progress visible elsewhere.

What is needed is a more general appreciation of the value of high scientific education by our manufacturers and leaders of industry. It is true that things are improving, and in proof of this I may state that many of my former students at Owens College occupy now places of trust and importance in various departments of chemical industry. But the demand for highly educated men is still small. It has been said that manufacturers can buy the scientific aid which they need: of course they can. What we as teachers and as chemists have to deplore is that, as a rule, they do not buy it; or, at least, they offer but a poor price for the article. In Germany a young man devotes six or seven years of his university course to the study of chemistry, because he knows that there is a good prospect of his obtaining a remunerative position afterwards. At the celebrated colour works at Höchst, near Frankfurt, my friend Dr. Pauli has somewhere about a hundred well-educated university men working at research or conducting the various departments of his business, and these receive salaries ranging from £250 to £500 per annum; and you may be sure that the directors at Höchst do not pay these salaries without getting a very good return for their money.

Our English laboratories and our English professors are as fully competent to turn out a finished article as are our German friends; but if the article is not in demand there is not much inducement to manufacture it. Then, again, the raw material must be good, and it is an unfortunate fact that in this respect the Germans excel us. They have a recognised national system of secondary education: we have none. The students entering at a German university have gone through a severe and prolonged school education. Those coming to our colleges to be made chemists are too often innocent of anything that can be with truth termed secondary education. To remedy this evil, to "organise our secondary education," is the first step towards attaining the position which the higher scientific education occupies in Germany. It is to be hoped that the recommendations of the Royal Commission, of which I had the honour to be a member, will form the basis of a measure to be brought forward in Parliament next session.

But meanwhile what is to be done? Surely we must continue to urge upon the Government that more substantial aid be granted than hitherto has been the case to places where the highest scientific instruction is given, and amongst these the college in the halls of which we are assembled is one of the most deserving.

What, then, we really need at present is a recognition by the State of the necessity of this highest form of scientific education. It is quite true that a large sum of money, about £740,000 a year, is now devoted to what is called "technical instruction," but the greater part of this money is now spent—some may think rightly, though others be of an opposite opinion—in the furtherance of less advanced instruction than is needed for striking out new paths in science. That our craftsmen should be brought up to the level of the requirements of the day is right and proper, and therefore I for one have always upheld the establishing of technical schools throughout the country, even if they did not attempt to do everything. But this technical education of the masses being thus cared for, the equally—or perhaps the more—important national duty of seeing that proper provision is made for those who are to be the future leaders of industry must be attended to.

Whether this can be best accomplished at the older universities, or whether we are rather to look to the younger seats of learning and of research now scattered over the country is an open question. All I desire to intone now is that our legislators and statesmen, as well as the public at large, should be made aware of our national deficiencies, and take to heart the necessity—if England is to retain her supremacy in trade and industry—of making due provision, somehow and somewhere, for that highest training in science which ensures discovery and progress, and upon the application of which all our industries depend.

THE DURATION OF X-RADIATION AT EACH SPARK.*

By FRED. T. TROUTON.

THE object aimed at in this investigation was to ascertain how long a Crookes tube continued at each spark to give out Röntgen radiation.

The method adopted was to rotate a metallic toothed wheel—cut out of zinc sheet—interposed between a tube of the "focus" pattern and a sensitive photographic plate protected from ordinary light actions. Only one spark is allowed to pass by making one brake of the primary.

The departure from sharpness of outline of the image of the moving teeth on development is observed, and measured in terms of the width of a tooth. If the speed of rotation is known, the length of time the effective radiations persists for can be at once deduced.

A mercury brake worked by hand was generally used. The tube was distant from the plate by about 8 centimetres. When the wheel is rotated sufficiently fast a drawing out of the image is always noticeable, but the amount of its drawing out in each case is found to vary in an important way with circumstances, and is probably but a measure of the length of time the E.M.F. remains above the value necessary for discharge, and thus depends ultimately on the arrangement used—the coil, &c.

If a spark gap in parallel with the tube be provided, the drawing out is cut short on the presence of a spark. How early this occurs depends on the distance apart of the sparking points. In this way comparatively sharp-looking images are obtainable at high speeds of rotation of the toothed wheel, without otherwise altering the arrangements.

* Read before the British Association (Section A), Liverpool Meeting, 1896.

The length the radiation lasted for, measured from photographs obtained in this way, varied continuously from about 1-800th of a second, when no parallel spark is allowed to occur, to 1-10,000th of a second, obtained with the sparking points the nearest possible consistent with getting any effect at all.

These experiments can also be made using a phosphorescent screen. The measurements are not capable of being made with the same certainty, but it is a more convenient way to observe the action of the early cut-off by a parallel spark on advancing or retreating the spark points.

CONSTITUTION OF THE CARBOHYDRATES OF CEREAL STRAWS.

FURTHER REPORT OF INVESTIGATIONS.*

By C. F. CROSS and CLAUD SMITH.

IN the Report already furnished to the Committee we have called attention to the results contained in our paper in the *Journ. Chem. Soc.*, 1896. This work, as explained, occupied us from September of last year to the date of publication.

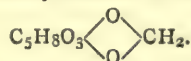
It was also stated that, having elucidated in general terms the constitution of the furfuroids of the *Cereal Celluloses*, and also devised a simple method of separating these constituents, we were about to apply the results and methods to the growing crops (barley) of 1896.

We now have to report that these observations are concluded, and have furnished positive results.

It was shown that the furfuroids of the celluloses from the mature straws had the following characteristics:—

1. The empirical composition of the celluloses, $C_{10}H_{10}O_5$.
2. Yield with phenylhydrazin, however, the osazones *not* of hexoses, but of pentoses (xylose).
3. Yield with hydrogen peroxide, on warming, a characteristic decomposition with formation of a large quantity of CO_2 .

These results are generalised in a formula showing a pentose and formaldehyd residue in combination, thus:—



4. The compound, as isolated by acid hydrolysis, is partially fermented by yeast in neutral solution; the solution after fermentation shows a disappearance of about 50 per cent of the furfuroid.

Applying these methods to the diagnosis of the furfuroid of the *growing plant*, we have established the following points:—

1. The furfuroids are separated by hydrolysis with 1 per cent H_2SO_4 at 3 atm. steam pressure.
2. *Osazones*.—In the early stages the osazones obtained from the products of such hydrolysis show *high melting-points*— 180° to 190° . They are *not*, therefore, pentosazones (which melt at 145° to 155°), but probably hexosazones.
3. *Fermentation* (Yeast).—Up to the flowering period the plant yields, to acid hydrolysis, furfuroids which are *readily and entirely* broken down by yeast.
4. *Hydrogen Peroxide reaction*.—The furfuroids, up to the flowering stage, yield *no carbonic acid* on treating with the reagent at 80° to 95° .

These results differentiate positively the furfuroids of the young growth from the *pentoses*, and also from the *formal-pentoses* of the mature stem.

In growth, from the *flowering period onwards*, we are

* Read before the British Association (Section B), Liverpool Meeting, 1896.

able to diagnose a progressive attainment of the constituent features which belong to a *pentose-formal*.

Osasones.—The melting-points are progressively less: those isolated from products from plants cut on July 14th have a melting-point 176° to 178° ; on August 14th the osasones had the m.p. 125° to 129° .

Fermentation.—The furfuroids of July 14th were fermented to the extent of 80 per cent; August 4th 70 per cent; August 14th 55 per cent.

H₂O₂ Reaction.—The first appearance of the characteristic decomposition, with evolution of CO₂, was noticed in the furfuroids from plants cut on August 4th, yielding 4.0 per cent CO₂; on August 14th the quantity had increased to 5.5 per cent.

It will be remembered that the celluloses from the mature straws give furfuroids yielding 21 per cent CO₂.

These results will be published in full in a forthcoming paper to the Chemical Society.

Recorded here in abstract, they are sufficient to show that our investigations have been productive of positive results, and are based upon a method of attack of the problems involved which is capable of useful extension.

We have now to call attention to conclusions of more general import, and to forecast some developments of our views of *assimilation* in plants.

Our observations on the crops of 1894-5 were directed to estimating the following:—

1. Percentage of furfural obtainable (a) from entire plant, (b) from its permanent tissue. The proportion a : b measured the percentage of *easily hydrolysable* furfuroids. This proportion is always small.

Incidentally we made observations on proportion of nitrogen, ash constituents, &c.

On re-calculating the results for the 1895 crop to nitrogen-free, ash-free substance, *i.e.*, to the carbohydrates of the plant, we find the percentage of furfural to *vary but little*. There is a maximum at the flowering period, but the range of variation is slight.

It will be remembered that the furfural (the measure of the furfuroids) is also independent of the conditions of soil nutrition, and but slightly influenced by extreme variations in the atmospheric conditions of growth.

Putting these facts together, they point very positively to the conclusion that the *furfuroids* are *direct* or *primary products of assimilation*. There is, of course, no reason in the nature of things why this should not be so; but our ideas have become so fixed upon starch, cane-sugar, or generally the normal hexoses, as the exclusive primary products, that there may be some objections raised to this conclusion on the presumption that it is improbable. The evidence we shall deal with in due course and in greater detail in our paper to the Chemical Society.

Another issue is raised by these observations. Resuming our statement that the assimilation of the barley plant results in the formation of normal hexose groups and furfuroids in the constant proportion of 4 : 1 (approximately), how are these distributed during the whole period of growth? Up to the time of ear-formation there is no great difference in distribution. But the cereals are characterised by the relatively large weight of seed which they produce. Thus in the growth of 1894-5 which we investigated, the following were the recorded yields of grain and straw:—

	PLOT 1.		PLOT 6.	
	Permanently unmanured.		Maximum fertilisation.	
	Grain.	Straw.	Grain.	Straw.
1894.	947	1291	2616	3774
1895.	415	606	1616	1831

The grain being almost constantly 40 per cent of the harvested plant, notwithstanding extreme variations of season and fertilisation.

The seed builds up starch as its preponderating constituent, and the furfuroids of the mature grain are correspondingly low.

After flowering, therefore, the furfuroids are chiefly appropriated to the stem tissues. The question, however, arises—Is this distribution, and more generally is the transference of matter to the seed, a direct process, or is it *indirect*? *i.e.*, Is it not possible that the stem tissues contribute to seed formation by *depletion* at the ripening stage? always admitting (for the moment) that both processes may be concurrent.

Upon this point we are accumulating evidence, and it appears probable that we may be able to establish this as a feature of the life-history of plants.

We may point out that the cereals are especially marked out for study of this question, by reason of the extremely high proportion of seed which they form, and also from the presence of furfuroids in large proportion, and fulfilling the rôle of a "constant" of the plant.

In our future investigations we shall attack this matter in various ways: by more careful observation of the total weight of the plant, and the variation of gross weight of stem and ear during maturation of the seed: next, by removing the flower and preventing seed-formation, noting the effect on the assimilation in the grass, and the relative assimilation of normal hexoses and furfuroids.

It will be evident, from this abstract and brief forecast, that we have taken advantage of the assistance given us by the Association, and that we have ample prospect of doing further useful work. Should the Association be able to continue the grant, we shall impress more help into the work and be able to compass a wider field.

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CHEMISTS AS LEADERS.

By PETER T. AUSTEN, Ph.D., F.C.S.

THE historians of human development speak of the Stone Age, the Bronze Age, the Iron Age, and other ages, meaning thereby the successive periods of human activity that have been characterised by the use of these materials. The most fitting term to apply to the period which began between fifty and a hundred years ago, and whose development is yearly more rapid and more wonderful, would be "The Chemical Age."

In the past, while what was called philosophy marked a high mental activity, much of it was a form of thought based almost entirely on abstract speculation, for the study of matter and its changes was almost unknown. Instead of the exact observation of material objects and their behaviour under varying conditions, and the study of the phenomena of Nature, all kinds of imaginative trains of thought were evolved, and speculations, often baseless, were put forward with little idea as to whether they were supported or not by facts. Even when facts were observed, they were often distorted in order to make them accord with the false or visionary philosophy of the day. But when the delicate balance was invented, and the weights of the different kinds of matter could be exactly determined, and their changes followed with precision, the great principle of the indestructibility of matter was established, and the schools of abstract philosophy suffered an overturn. Instead of the observed fact being subservient to the speculation, the observed fact became dominant, and speculative philosophy retained its value only so far as it accorded with and explained, or amplified by inference, the fact.

All this bears directly upon the conditions of modern competitive life. For instance, men, first of all, must obtain food. To obtain it from weaker communities by force or robbery could be successful only for a time, as the producers were either exterminated, or they gave up so unprofitable an industry. The food supply of mankind

depends on the application of a knowledge of the principles involved in plant growth. The basis of this knowledge is chemistry. It was not really until 1840 that it was demonstrated by the great chemist Liebig that plants, like animals, feed. They take certain kinds of nutriment out of the soil, and soon exhaust it. Soon they fail to grow. Liebig showed that if these nutritive substances were put back into the soil, the plants would keep on growing, and that there was no limit to the productiveness of the earth when properly nourished as chemical science indicated. Malthus stated that the population must be restricted, else it would exceed the food supply. Liebig showed that the production of food-stuffs, made possible by the application of chemical science, was so immense that such a danger is not to be feared. Chemical knowledge has rendered it possible to make several blades of grass grow where there was only one. Liebig then investigated live-stock and proved that, though animals eat many kinds of food, the food owed its value to a few definite nutritive elements that are found in greater or less amounts in all foods; and that the animals, though seemingly widely different in physiological nature, were composed essentially of the same substances. Thus the raising of live-stock and the production of dairy products were placed upon a scientific basis. Agriculture began to employ scientific methods and the cost of raising plants and animals was greatly reduced.

It is not always easy to appreciate at first glance the far-reaching effect of a chemical discovery. The introduction of the hot blast in the manufacture of iron increased the production of pig-iron. The invention by Bessemer of the converter method of making steel practically revolutionised the manufacturing industry of the whole world. What cheap steel means to humanity could not be told in a large volume. The invention of the basic process for treating phosphatic iron ores by Thomas and Gilchrist made it possible to produce steel from ores existing in immense quantities, and hitherto entirely worthless. And, strange to say, phosphorus, the "iron master's curse," is now obtained as a phosphatic slag, which is a most valuable fertiliser for the farmer. The chemist turned the bane of England's iron industry into a blessing to England's agriculture. Weldon utilised the waste product in the manufacture of chlorine, so that it could be used over and over again. In turn was reduced the price of bleach, of bleached white cotton, and of white paper. Books were made cheaper. Education was cheapened. The waste tars of the gas manufacture under the skilful hands of a host of chemists are now the basis of an immense industry. They produce brilliant dyes, perfumes, antiseptics, medicaments, and what not. The astonishing development of chemical knowledge has assisted in the evolution of electricity, the commercial future of which is incalculable. The study of life has been taken up, and by the aid of the colossal genius of Pasteur, disease in plants, animals, and men is checked and avoided, thousands of lives are yearly saved, and the tenure of human existence is far stronger than it was half a century ago. Many pages could be written to illustrate how far-reaching and how little short of marvellous have been the modern advances in chemical science and their applications. But they have taken place so quietly, although irresistibly, that the average individual does not appreciate the part they are playing; nor can we estimate the still greater part they are to play. Another striking instance of the results of chemical research is the development on the one side of explosives, and on the other of hard and tough steel. Without the assistance of the chemist war would be monotonous.

The stability of a community lies in its independence. Its independence is based on its productiveness. Manufacturing consists in changing one kind of form of matter into some other kind of form. It is easy to understand, therefore, that chemistry, the science that studies the changes in the identity of matter, underlies the manufac-

turing arts. Hence the industrial status of a nation may be fairly estimated by the condition of its chemical knowledge. It is fair to hold that the country that has the best chemists will, in the long run, be the most prosperous and the most powerful. It will have at the lowest cost the best food, the best clothing, the best manufactured materials, the fewest wastes and unutilised forms of matters, the best guns, the strongest explosives, the most resistant armour. Its inhabitants will make the best use of their country's resources; they will be the most healthy, the most free from disease; they will oppose the least resistance to favourable evolution; they will be the most thrifty and the least dependent on other nations. The education of its people in chemistry and the physical sciences is the most paying investment that a country can make. Competition to-day between nations is essentially a competition in the science and applications of chemistry.

It is fair to assume, also, that if men who have devoted their lives to the study and practice of chemical science, and who hence must have the clearest understanding of all men of the true relations existing both between material things and between material things and humanity, also possess the mental calibre that may enable them to be men of affairs, they ought to be especially successful in executive positions. Such an assumption is supported by the fact that the number of responsible positions, at first sight quite unconnected with chemistry, which at present are filled by chemists, or men who have received a chemical training, is large. This shows, not that the chemist is an unusual kind of man, but that a chemical education may make a man unusually efficient. Perhaps as striking an illustration of this as any is the increasing number of chemists in charge of large educational institutions. There is no position in which a man may more powerfully and so lastingly influence man than that of the head of a large school or college.

The Marquis of Salisbury, Prime Minister of England, is a chemist, and spends much of his spare time, when he has any, in his finely-appointed laboratory. And France now places in the most intricate and difficult of positions, that of Minister of Foreign affairs, her most eminent chemist, Berthelot.

These are signs of the time; indications of the chemical age that the world has now entered into, and in which it is destined to remain for many years to come. It will be interesting to watch the course of the two great nations which are now under the guidance of chemists—bearing in mind that Germany is now the home of chemistry, nor forgetting that Russia's advance in chemistry during the last quarter of a century may fairly be called phenomenal.

In this connection it may be pertinent to ask what has become of all the clever and earnest young Japanese chemists who have been studying at the leading educational centres of Europe and America during the last years.—*North American Review*.

ON ARGON AND HELIUM.

By SIEGFRIED FRIEDLÄNDER.

THE author concludes from his experiments and observations that—

1. Argon which was found incapable of reaction in the numerous attempts of its discoverers, of Berthelot, and of H. Moissan, reacts with platinum, as Troost and Ouyard had already shown for magnesium on the prolonged action of electrical discharges.

2. Helium is present in the atmosphere at Berlin, as it has also been previously shown at Bonn by Kayser. The quantity is extremely minute. If we consider that the total contents of the tube have to be absorbed, and that in spite of the enormous sensitiveness of spectral analysis the line was observed only with an extremely trifling

intensity, it will not seem exaggerated if we estimate the proportion of helium in the atmosphere as about about 1:1000 millions.

3. Helium reacts with platinum on the prolonged action of electric discharges. This has been already observed for magnesium by L. Troost and L. Ouyard. With aluminium, Bohuslav Brauner has inferred an absorption of helium.

That in the present case only the yellow line was observed is easily explained by the considerable difference in the intensities of the chief lines of helium.

It is remarkable that numerous argon lines lie very near to helium lines without being identical. This similarity in the spectra of the two gases leads us necessarily to the conclusion that the gases themselves must be similar in their behaviour. Now C. Lunge and F. Paschen have shown that helium is not an element, but a mixture of two substances, whence, from a parity of reasons, the inference seems justified that argon is not an element, but a mixture of probably two elements.

For this view the two following facts seem to speak. According to the researches of Lord Rayleigh and Prof. Ramsay the relation of the specific heats is found according to the well-known formula—

$$n\lambda = v = \sqrt{\left[\frac{e}{d} (1 + at) \frac{Cp}{Co}\right]} \text{ as } 1.61 \text{ and } 1.65.$$

Hence argon would be a monatomic element, and would have the atomic weight 40. But as an element with this atomic weight has no place in the periodic system, the monatomicity of argon has been called in question by several investigators. Thus, e.g., R. Nasini came to the conclusion that we must either reject the results of the kinetic theory of gases or overturn the periodic system. Or, if we assume argon as a diatomic element with an atomic weight equal to its vapour density, with this atomic weight we should uphold the accuracy of the periodic system, but should sin against the kinetic theory of gases, whose conclusions have hitherto shown themselves worthy of recognition. The only remaining assumption is that argon may possibly be not an element—an assumption which has been already convicted by its discoverers.

Crookes has hitherto pointed to the possibility of the compound nature of argon, in reliance upon spectroscopic investigation. J. M. Eder and E. Valenta consider this view as not excluded. But whilst the last-mentioned investigators have examined only the red spectrum of argon, Crookes has observed both spectra, of which the red one is best visible at the pressure of 3 m.m. and at a reduced pressure changes into the blue. Crookes has shown that it is not easy to obtain the blue spectrum quite free from the red, whilst in some circumstances the red spectrum does not change into the blue. Armstrong, indeed, thought this need not be recognised as an evidence of the composite character of argon, since also nitrogen, hydrogen, and oxygen display such spectra. But as hitherto in these elements both spectra have never been seen simultaneously, Armstrong's view need not be accepted as a strict proof of the elementary nature of argon. I myself regard the phenomenon observed, that both the spectra of argon appear simultaneously, as one of the weightiest proofs that Lord Rayleigh and Prof. W. Ramsay have revealed two new elements by their discovery of argon.—*Zeitschrift für Physikalische Chemie*, vol. xix., p. 657.

The Cattle Plague in Africa.—Dr. Edington calculates that £1,000,000 will have to be expended before this scourge is overcome. It was introduced by the Italians, who imported diseased European cattle into their colony at Massowah. It was conveyed up the Nile valley by the Arab caravans, reaching Kilema Njara in 1893. Elephants have been attacked as well as oxen and buffaloes.—*Indian Pharmacologist*.

SEPARATION OF OZONE FROM HYDROGEN PEROXIDE, AND RECOGNITION OF OZONE IN THE ATMOSPHERE.

By C. ENGLER and W. WILD.

As we have already mentioned in a former communication, chromic acid decomposes energetically hydrogen peroxide, even in the most dilute state, both when the chromic acid is used as a solid, distributed on glass beads, and when applied as a concentrated solution.

We have ascertained by special experiments that chromic acid, either in the solid state or in solution, allows the passage of ozone unchanged. Comparative determinations of the percentage of ozone directly and after passage through chromic acid (effected by titrating the iodine liberated from potassium iodide) gave results perfectly accordant; the discrepancies, distributed quite irregularly, were within the limits of experimental error. If we passed through the chromic acid tube, to which was connected by fusion a J-tube with glass cocks, from the one side a strong current of air which had passed through very concentrated hydrogen peroxide heated to 70°, and carried with it considerable quantities of the latter; and from the other side a slow current of oxygen containing a trifling proportion of ozone, ozone was always easily recognised after the chromic acid. But there was found no trace of hydrogen peroxide, even by means of the most sensitive reaction—the mixture of ferric chloride and potassium ferricyanide. The same result was obtained if we put into a glass flask a little concentrated hydrogen peroxide and some ozoniferous oxygen, and, after previous shaking, sucked it off through a chromic acid tube.

In these experiments we had again opportunity to observe that the mutual decomposition of ozone and hydrogen peroxide in a dilute state ensued very slowly, and that both may be present together for a long time. Nothing could be perceived of an absorption of ozone by the chromic acid modified by hydrogen peroxide.

From these experiments chromic acid appears a suitable agent for deciding the question of the presence of ozone in the atmosphere. This question has been often ventilated, but it has not been decided on account of Schöne's discovery of the presence of hydrogen peroxide in the air. For the decision of this difficult question there are two possibilities. We either employ a reagent which is affected by ozone alone, and not by other constituents occurring in the air, or we first remove those substances which might give the same reaction as ozone; therefore above all hydrogen peroxide, and, in case of certain reagents for ozone, nitrous acid also. The first and simplest method is impeded by the want of suitable reagents, since the reaction hitherto considered as exclusively characteristic of ozone—i.e., the formation of black silver peroxide upon a bright plate of silver—is far from being sufficiently sensitive. However, according to our experiments, paper steeped in a concentrated solution of manganese chloride is suitable for the certain detection of ozone when its change is tested by moistening with tincture of guaiacum.

Ozone turns such paper brown in consequence of the formation of manganese dioxide, whilst hydrogen peroxide—or nitrous acid—has no such effect. The objection was urged by Schöne against the manganese papers that a brown colouration is produced also by means of ammonia and ammonium carbonate. This is quite correct; but the browning produced by the separation of manganese oxide and its oxidation is easily distinguished from that due to ozone. The latter, namely if moistened with solution of guaiacum resin, turns at once blue. The blueness, indeed, appears (as with thallium papers) even before the browning is visible if ozone has been active. But the browning produced by ammonium carbonate yields no such blueness. It scarcely requires mention that the presence of free halogens, hypo-

chlorites, &c., must be excluded, since they produce the same reaction.

As for the use of this paper for the determination of ozone in atmospheric air, it seems not sufficiently sensitive, and is in this respect inferior to thallium papers, as they in turn are inferior to potassium iodide starch paper. We prefer, therefore, for the present the second way, and in the first place seek to remove the hydrogen peroxide, by allowing the air to pass first through a tube with chromic acid distributed on glass beads, and then test for ozone on receivers with the different reagents for the ozone. Further experiments must decide whether the traces of ozone which can occur in experiments with atmospheric air pass through when the chromic acid is partially reduced to chromium oxide.—*Berichte*.

A GENERAL METHOD FOR OBTAINING THE METALLIC HYDROXIDES ELECTRO-CHEMICALLY.

By RICHARD LORENZ.

THOUGH it is a very customary reaction to precipitate metallic salts with potassa or soda lye, this procedure is not very well suited for the preparation of the hydroxides. When obtained in this manner they are not readily purified by washing, as they retain obstinately a considerable quantity of alkali-hydroxide. A number of hydroxides are very freely soluble in alkaline lye. These (as *e.g.*, chromium hydroxide, zinc hydroxide, &c.) are consequently not easily obtained in this manner.

These defects may be easily evaded.

In order to obtain certain hydroxides electro-chemically there has been hitherto proposed the electrolysis of saline solutions, the chlorides being indicated as the most suitable. If we, *e.g.*, electrolyse a solution of magnesium chloride between platinum electrodes, hydrogen is separated out and magnesium hydroxide is liberated at the kathode. This method seems to have no prospect as a preparative process. It must be pointed out that in salts with anions which do not escape, such as sulphates or nitrates, the use of diaphragms is necessary. Nevertheless the yield of hydroxide is defective on account of diffusion.

Even in the case of chlorides the anion occasioned difficulties. The anodic chloride dissolves in the electrolytes and occasions disturbing by-reactions. Chlorine and metallic hydroxides form hypochlorites. The electrolytic process of bleaching depends on the technical utilisation of this secondary process. Hermite, *e.g.*, submits to electrolysis a mixture of a solution of magnesium alkali-chloride with magnesia, or a mixture of magnesium and calcium chlorides and magnesium hydroxide, and obtains thus his well-known bleaching liquid. These conditions reappear on the electrolysis of chlorides in the laboratory. If, *e.g.*, an excess of magnesium hydroxide is liberated, magnesium hypochloride may readily be formed at the anode.

A third defect of the procedure is the formation of hydroxides at the kathode. The consequence is that the kathodes are generally coated with a non-conductive layer, which may even lead to an interruption of the current. In technical preparation knives are even fixed at the kathodes, which scrape off the incrustations formed.

Finally, this method is very limited. It can serve only for the production of the hydroxides of such metals whose tension of decomposition is greater than that of water. It relates almost exclusively to the production of the hydroxides of the alkaline earths. But if we electrolyse, *e.g.*, solutions of copper or of nickel, the metal separates as such on the kathode, hydroxides not being found at all.

In fine we have, therefore, for the production of metallic hydroxides, a chemical method (precipitation with an alkaline hydroxide) which is general but defective, and an electro-chemical, which is neither general nor useful.

A perfectly universal electro-chemical method, which yields good results, is the following:—We select, according to the conditions of the case, a bath of potassium or sodium chloride, sulphate, or nitrate, and immerse in it a kathode of platinum and an anode of the metal whose hydroxide we seek to obtain. The anion travels to the anode and dissolves it. If we apply, *e.g.*, an anode of cadmium in potassium chloride, there are formed cadmium ions at the anode. Around the kathode there are formed hydroxyl ions by the secondary process. If we agitate the liquid, cadmium hydroxide is deposited in an insoluble precipitate. Even if we were not to agitate, cadmium hydroxide would be gradually formed. The cadmium ion would travel towards the kathode, and on the encounter the hydroxyl ions travelling towards the anode would be precipitated along with them.

This method presents the following advantages:—

1. All the hydroxides insoluble in water may thus be obtained, whether they are soluble in an excess of alkali or not (chemical method), or whether the metals decompose water or not (former electro-chemical method). There are formed hydroxyl-ions and metal-ions in equivalent quantities; thus the hydroxide sought for appears as a precipitate in the neutral solution of an alkaline salt.

2. The precipitate of metallic hydroxide is formed neither at the anode nor at the kathode, but in the solution, like the precipitate from a chemical reaction, but without the reagent.

The consequence is that no coatings are formed at the kathode, the current is not interrupted, and large quantities of precipitate can be separated with the same conditions of current and the same concentrations of the electrolytes.

3. Because the precipitates are formed without the use of a reagent nothing can adhere to them, and they must therefore be distinguished by great purity, supposing the anodes to consist of pure metal. Only the electrolyte used can adhere to them, but an alkaline salt is much more readily washed out by hydroxides than is an alkaline hydroxide.

4. The yield of all hydroxides is very complete, and is almost uniform. The only limit is the solubility in water.—*Zeitschrift für Anorganische Chemie*, xii., p. 436.

ON THE COLOUR OF THE ALCOHOLS COMPARED WITH THAT OF WATER.

By W. SPRING.

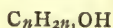
OUR knowledge on the relations between the chemical structure of a substance and its colour leaves still much to be desired.

We can indeed establish that certain atomic groups, called on that account chromogens, communicate a more or less intense colour to organic bodies; but we must admit that we know very little or nothing concerning the colourations displayed by the members of the simplest organic homologous series.

This gap in our knowledge is doubtless founded in the opinion that most organic bodies are colourless. They appear so, in fact, if they are viewed in strata of such thickness as occur in ordinary operations; but this is no evidence that colouration does not appear if we examine the substances in strata of such depth as to make the absorption of the light directly perceptible. A research conducted on this point of view has the same scientific interest as the determination of any other physical attri-

bute of compound belonging to one and the same homologous series. Such an investigation will doubtless lead to conclusions of value for the explanation of the general properties of matter.

These considerations led me to examine the question whether the monovalent alcohols of the formula—



are coloured or not. This class of bodies has been chiefly selected because their chemical properties already known show them to be higher homologues of water, and because the last substance appears colourless only in thin layers. Like water, the alcohols contain in their molecule a constant group, hydroxyl —OH; they are distinguished from water by the fact that they contain a hydrocarbon radicle increasing continually from one compound to the next. This is clearly shown by the following formula:—

HOH.	Water.
CH ₃ OH.	Methanol.
C ₂ H ₅ OH.	Ethanol.
C ₃ H ₇ OH.	Propanol, &c.

Another reason which decided me to choose this class of substances lies in the possibility that its members, CH₃OH, C₂H₅OH, and C₃H₇OH, can be cheaply produced in large quantity and of unquestionable purity.

The Experiments.

For observing the colour of the alcohols I made use of the two tubes, 26 metres in length (*Bull. de l'Acad. Roy. de Belg.*, 1896, iii., 31, 95—110), the construction of which is described in my paper "On the Part played by the Currents of the Convection of Heat in the Illumination of Clear Water." One of the two tubes was kept always full of pure water for comparison. The other tube received the various alcohols successively. Neither of the three alcohols examined is colourless in a stratum of 26 metres. Methyl alcohol had a blue colour, slightly inclining to green, as also ethyl alcohol, but with a colder tone. Amylic alcohol is of a greenish yellow. The totally pure blue colour of water changes therefore regularly, becoming more and more mixed with yellow as we ascend in the homologous series.

In the spectrum of water the red is little pronounced, the yellow is expelled, the green very bright, the blue complete, whilst the violet is only transmitted partially. The same property is observed in the spectrum of the alcohols, but the absorption in the violet increases more and more the more the carbon chain predominates, whilst the decrease in the red is little perceptible. The hydroxyl group —OH effects the absorption of the extreme red in the spectrum, and the carbon chains extinguish the opposite end (violet and blue) in dependence on the number of the carbon atom.

Water, H.OH, containing no carbon transmits much violet, methyl alcohol less, and amyl alcohol shows the first blue visible in the spectroscopic; nothing is to be seen in the violet. Red remains equally visible in the four substances. The spectrum of ligroin consisted of only three colours—green, orange, and a little red. We may even maintain that the alcohols possessing more than 5 atoms of carbon will include among themselves compounds which entirely extinguish the blue of the solar rays.

The few observations which form the subject of this communication raise several questions the solution of which will not be without interest. Is the tone of the blue colour of an alcohol related to the number of hydroxyl groups of the molecule, *i. e.*, are the polyvalent alcohols more blue than the monatomic? What is the rôle of the aldehydic or ketonic hydrogen in colouration? What is the influence of the substitution of the hydrogen of a hydrocarbon of any atoms or groups?—*Zeitschrift für Anorganische Chemie*, vol. xii., p. 258.

THE REMOVAL OF SILVER AND GOLD FROM SEA-WATER BY MUNTZ METAL SHEATHING.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

AMONGST the writers upon the occurrence of silver in sea-water, we have Malaguti, Durocher, and Sarzeaud in 1850, Fred. Field in 1856, and Forchhammer in 1865, and as it is difficult for many, especially in this part of the world, to obtain or see the originals, I quote the following extracts from their papers. None of them make any mention of the presence of gold in sea-water or of its removal.

The following extract is from a paper by Messrs. Malaguti, Durocher, et Sarzeaud, entitled—"Recherches sur la présence du plomb, du cuivre et de l'argent dans l'eau de la mer et sur l'existence de ce dernier métal dans les plantes et les êtres organiques" (*Fourm. Chem. Soc.*, iii., 1851, p. 69, extracted from *Ann. Ch. Phys.*, [3], xxviii., 129):—

"*Estimation of Silver in Sea-water.*—A considerable quantity of sea-water was taken from off the coast of St. Malo, a few leagues from land, and preserved during the course of the experiments in a wooden cistern, from which it was taken out as occasion required in glass vessels. The presence of silver in this water was first demonstrated by the sulphuretted hydrogen process above described; but in order to obtain a more exact estimation of the quantity 50 litres of the water were evaporated to dryness, and the crude salt thence obtained, weighing 1300 grms., was divided into thirteen equal portions, and each portion fused with 30 grms. of pure litharge and 1·13 grm. of lamp-black. This mixture, which was made very intimate by long trituration in a porcelain mortar, was gradually heated to dull redness in a crucible, and maintained at that temperature for fifteen or twenty minutes; the heat was then gradually raised till the mixture fused, and afterwards increased to whiteness; as soon as that temperature was attained, the crucible was withdrawn from the fire. Thirteen operations of this kind yielded 124 grms. of lead, and the silver contained in this was found by cupellation (deducting that which was yielded by the lead alone in a test experiment) to amount to 0·0005 grm. Now, as this demi-milligram of silver was extracted from 50 litres of sea-water, it follows that 100 litres—or, for simplicity, say 100 kilograms. of sea-water—contain 1 m.grm.; hence the proportion of salt in sea-water is, approximately, one part in 100,000,000, so that a cubic myriametre of sea-water contains 1000 kilograms., or a cubic mile (English) contains about 2½ lbs.† avoirdupois. This estimation must be regarded as a minimum; for all the preceding operations are attended with slight loss."

In the same paper they refer to the presence of silver in certain fuci, amounting to 1/100,000; in various trees, such as oak, birch, beech, and apple, also in the blood of an ox and the vegetables upon which it has been fed. They also found it in rock salt and in coal, but as the coal contained pyrites, they do not attach the same importance to its presence in this case.

"On the Existence of Silver in Sea-water," by Frederick Field, F.C.S. (*Proc. Royal Society*, London, vol. viii., 1856-7, p. 292). He examined the sheathings of certain traders as follows:—

"*Ana Guimaraens*, a Chilian vessel, trading up and down the South Pacific for seven years. Yellow metal from the bottom of vessel; 5000 grains were dissolved in

* Read before the Royal Society of N. S. Wales.

† The amount obtained by Malaguti, viz., 0·0005 grm. of silver from 50 litres of sea-water, represents over 40 tons of silver per cubic mile, not 2½ lbs. only, as given in the above translation. Malaguti is not responsible for this error, as it does not occur in the original, where, however, there is also a great error, since 0·0005 g. for 50 litres is said to be equal to 1000 kilos. of silver per cubic myriametre instead of to 10,000,000 kilos.

pure nitric acid and the solution diluted; a few drops of hydrochloric acid were added and the precipitate allowed to stand for three days. A large quantity of white insoluble matter had collected by that time at the bottom of the beaker. This was filtered off, dried, and fused with 100 grs. pure litharge, and suitable proportions of bitartrate of potash and carbonate of soda, the ashes of the filter also being added. The resulting button of lead was subsequently cupelled and yielded 2·01 grs. silver, or 1 lb. 1 oz. 2 dwts. 15 grs. troy per ton. A piece of new yellow metal with which the vessel was being repaired yielded only 0 oz. 18 dwts. to the ton.

Nina, a brig just arrived in the Pacific from England. The experiments were performed as before with results:—1700 grs. of the new metal kept in the cabin for possible repairs gave 0·051 gr. = 0·003 per cent = 19 dwts. 14 grs. per ton; 1700 grs. from the hull, where it had been three years, gave 0·400 gr. = 0·023 per cent = 7 ozs. 13 dwts. 1 gr. per ton.

The amount of silver in the new metal for the *Nina* and *Ana Guimaraens* are unusually low, both being under 1 oz. per ton.

Bergman.—A piece from the hull gave 5 ozs. 16 dwts. 18 grs. per ton; a piece from the cabin gave 4 ozs. 6 dwts. 12 grs. per ton.

Parga.—200 grs. from a piece from the hull gave 0·072 grain, and a piece of fresh metal 0·050.

Grasmere, only coppered a few months.—610 grains from hull gave 0·075 and from the cabin 0·072 grain.

Mr. Field remarks:—"It will be observed that the amount of silver in the above specimens of fresh metal is very high, and it is probable that most of these are merely the re-rolling of masses of metal melted down from old sheathing, and have derived the greater part of their silver from the sea on former occasions. It is well known that the copper used in the manufacture of yellow metal is very pure, containing 2 or 3 dwts. of silver per ton, frequently not so much, and silver is very seldom associated with the other constituent, zinc. In order to arrive at more certain results, however, I have granulated some very pure copper, reserving some in a glass stoppered bottle, and suspended the remainder (about 10 ozs.) in a wooden box perforated on all sides, a few feet under the surface of the Pacific Ocean. When occasion offers, the box is towed by a line at the stern of a vessel which is trading up and down the coast of Chili. It is almost too soon to expect any decisive results at present, but in a few months I hope to be enabled to send both the original copper and that which has been exposed to the action of the sea."

I do not know whether Mr. Field ever published the results, but I have not come across any reference to them.

"On the Composition of Sea-water in different parts of the Ocean," by Professor Georg Forchhammer (*Phil. Trans.*, 1865, pp. 211, 212):—

"*Silver*.—Malaguti first showed that silver occurs in the organisms of the sea; I have subsequently proved it to exist in a coral, a *Pocillopora*, and several chemists have since tried to prove that silver is precipitated by the galvanic current between the copper coating of a vessel and sea-water. If the last determination is confirmed, the existence of silver in sea-water is proved by direct experiment. From the *Pocillopora alicornis* I have separated it in the following manner:—I dissolved the coral in muriatic acid, precipitated the solution by hydro-sulphate of ammonia, and dissolved the precipitate, which consisted of sulphurets, of phosphate of lime, and fluoride of calcium, in very weak cold muriatic acid, which left the sulphurets of silver, lead, and copper probably mixed with those of cobalt and nickel. These sulphurets were separated from the solution, evaporated to dryness with a little nitric acid, to which were added a few drops of muriatic acid, and dissolved in water, which leaves sulphate of lead and chloride of silver undissolved. When the filter which contained the latter substances is

burnt, the silver is reduced to metal; a solution of pure soda will dissolve the sulphate of lead and leave the silver, which, when dissolved in nitric acid, can be tested with muriatic acid. I obtained from *Pocillopora alicornis* about 1-3,000,000, or from a solid cubic foot of the coral about half a grain of silver."

Old Muntz Metal Sheathings.

Mr. Cecil W. Darley, late Engineer-in-Chief for Harbours and Rivers, was kind enough to obtain for me some pieces of old Muntz metal sheathing from the piles of wharfs undergoing repair. These were examined for gold and silver with the results given below.

The method used for assaying was as follows:—In each case 2000 grains, except where otherwise stated, of the sheathing in strips were dissolved in 1500 c.c. of pure nitric acid (1 to 3 aq.), free from chlorine. After being cut into strips, the sheathings were boiled in water, beaten, and scrubbed with a brass scratch-brush, so as to get rid of the dirt and scale as far as possible: this probably also had the effect of removing part of the portion richest in gold and silver, as the assays of the separated scale show that it contains more of the precious metals than the body of the sheathing. In most cases the residue was grey and contained much lead. The clear nitric acid solution was decanted and filtered off, and some sodium chloride solution added to ensure the precipitation of all the silver; in the few cases where there was an additional precipitate of silver chloride, this was added to the gold and other insoluble matter on the filter. The solutions varied from green to blue. The filter and residue were dried, wrapped in special assay lead free from gold, scorified, cupelled, and checked in the usual way. In certain cases the sheathing was dissolved in sulphuric acid (but, as the solution took place more rapidly in nitric acid, the latter was preferred), when a yellow substance was generally found on the clock glasses used for covering the beakers; this was found to consist of sulphur containing a little copper, the latter carried up mechanically by spiriting; the sulphur was doubtless derived from the sulphuric acid by part of the acid being reduced by the nascent hydrogen given off from the zinc of the alloy, or more probably by the reaction between the hydrogen sulphide and sulphur dioxide evolved.

Sheathing from an old trader, purchased in Sydney about 1874. The solution was made in sulphuric acid as already mentioned.

Silver, 4 ozs. 15 dwts. 9·2 grs. Gold, 1 dwt. 2·4 grs. per ton.

This sheathing was referred to in a paper on the "Origin of Gold Nuggets" (*Trans. Roy. Soc. N.S. Wales*, 1893, p. 331), and was remarkable for containing a good deal of iodine; but none of the other sheathings, since examined, have yielded any iodine.

(a) From pile in Mr. Thomas Nobbs's wharf at Ballina, N.S. Wales, between high and low water mark. Exposed four years to sea-water. Corroded, but not so deeply as (d).

2000 grains gave—Silver, 6 ozs. 9 dwts. 8 grs.; Gold, 11·8 grs. per ton. Metallic copper, 64 per cent.

(b) From longitudinal brace in Ballina Government wharf, N.S. Wales, between high and low water mark. Exposed six years to sea-water.

2000 grains gave—Silver, 2 ozs. 2 dwts. 22 grs.; Gold, 4·7 grs. per ton. Metallic copper, 64 per cent.

(c) From piles in Government wharf, Ballina, N.S. Wales, between high and low water mark. Exposed six years to sea-water. Not much corroded and fairly thick metal.

2000 grains gave—Silver, 3 ozs. 19 dwts. 5 grs.; Gold, 19·6 grs. per ton.

2158 grains gave—Silver, 4 ozs. 5 dwts. 14 grs.; Gold, 1 dwt. 7 grs. per ton.

2394 grains gave—Silver, 4 ozs. 12 dwts. 0 gr.; Gold, 1 dwt. 22 grs. per ton. Metallic copper, 60·3 per cent.

In the last the solution was made with sulphuric acid.

(d) From the pile of Mr. Fenwick's wharf, Ballina, N. S. Wales, wholly submerged for thirteen years in sea-water.

So brittle as to break readily between the fingers, with a copper-coloured granular fracture; hence in parts most of the zinc has apparently been dissolved out. The sheet is much corroded, and very thin on the edge, stained green and brown.

Heated in a tube it emits a "sea-shore" odour, and gives off water which has an acid reaction; it also yields a fusible sublimate of tarry matter mixed with sulphur. Dissolves entirely in nitric acid, one to three water. The metal when boiled with water yields a solution containing chlorine and a trace of sulphuric acid from sulphates. After boiling with pure dilute sulphuric acid, the metal acquires a copper-red colour and shows a granular or crystalline structure; a black residue is left, and the solution, on cooling, deposits crystals of lead chloride.

2000 grains gave—Silver, 3 ozs. 14 dwts. 21 grs.; Gold, 9 grs. per ton. Metallic copper, 62·2 per cent.

The scale, first treated with nitric acid:—

227 grains gave—Silver, 1 oz. 10 dwts. 4·4 grs.; Gold, 15 dwts. 19·5 grs. per ton.

(e) From Irvington, N. S. Wales. Exposed to fresh water; very little corroded.

2000 grains gave—Silver, 5 ozs. 6 dwts. 8 grs.; Gold, 19·6 grs. per ton. Metallic copper, 62·3 per cent.

The scale, extracted with nitric acid, and the residue scorified and cupelled:—

70 grains gave—Silver, 1 oz., 7 dwts. 23·10 grs.; Gold, 9 dwts. 8·22 grs. per ton.

(f) From Coraki, N. S. Wales. Exposed to brackish water.

2000 grains gave—Silver, 5 ozs. 6 dwts. 12 grs.; Gold, 13 grs. per ton. Metallic copper, 63·5 per cent.

(To be continued).

BACTERIAL ACTION OF POTASSIUM PERMANGANATE, CHROMIC ACID, AND IODINE.

By ROBERT MELDRUM, F.C.S.

THE following experiments were made with Loch Katrine water to which was added about one-tenth c.c. of urine per gallon and allowed to incubate from 12 to 48 hours. When the water was judged to be sufficiently rich in bacteria, the sample was well agitated and the number of colonies present ascertained. The culture medium employed was that recommended by Frankland, viz., one litre of extract from one pound of lean meat, 100 grms. gelatin, 10 grms. peptone, 5 grms. salt; the acids present being neutralised with caustic soda. The incubations were conducted for four days at about 75° F. Petrie dishes were adopted instead of plates. For every series of cultivations blank experiments were also made, but with negative results. The temperature during time of contact would be about 60° to 65° F.

Out of a total of 32 experiments it will be noted that complete sterilisation only resulted in two cases. It is remarkable that a strength of 42 grains per gallon of such a powerful oxidiser as potassium permanganate should not produce complete oxidation of such minute organic bodies even in five minutes, whereas a strength of nearly one-sixth of that should produce nearly complete sterilisation. This uncertain action is not uncommon to the salts investigated, and may probably be explained by (1) an excessive quantity of soluble organic matter being present which consumes the greater part of the salt before it has time to exert a destructive action on the organisms; or by (2) the presence of bacteria in the internal parts of both organised and unorganised particles which are present in the water, and in this way being protected from the action

Bacterial Action of Permanganate.

Grains of Permanganate per gallon.	Colonies of Bacteria per c.c. before treatment.	Colonies of Bacteria per c.c. after treatment.	Time of contact in minutes.	Remarks.
1·4	Innumerable.	Innumerable.	5	Gelatin
1·4	"	"	5	liquid.
2·8	"	"	5	in 48
2·8	30,000	300	5	hours.
2·8	1000	10	10	
7·0	Innumerable.	Innumerable.	5	Gelatin becomes
7·0	"	"	5	liquid.
7·0	"	"	5	Gelatin becomes li-
7·0	30,000	200	5	quid. Cols.
7·0	6000	80	10	mostly
7·0	"	50	20	pin head.
7·0	1400	60	30	Nearly all
7·0	"	40	40	chromo-
7·0	"	25	60	genic
7·0	2000	100	5	colonies.
7·0	"	9	10	
7·0	Not determined.	0	10	Chromo-
7·0	1000	15	10	genic
7·0	"	4	20	colonies.
7·0	300	4	5	
7·0	"	3	10	
7·0	"	3	30	
14	30,000	100	5	Pin head
14	"	120	5	colonies.
14	1400	60	10	Some cols.
14	"	40	20	chromo-
				genic.
21	60,000	100	5	Nearly all
21	"	130	5	liquefy gel-
				atin.
32	1000	3	10	Mostly pin
32	"	0	20	head cols.
33	6000	200	5	All chro-
42	"	200	5	mogenic.
				Liquefies
				gelatin.

of the reagent for a considerable time; by (3) the life-history of the organisms. The latter theory is the more likely.

Bacterial Action of Chromic Acid.

Grains of Chromic Acid in gallon.	Colonies of Bacteria per c.c. before treatment.	Colonies of Bacteria per c.c. after treatment.	Time of contact in minutes.	Remarks.
7	About 30,000	2000	10	Nearly
14	"	3000	10	all
28	About 2000	100	10	pin head
28	"	10	10	colonies.

Bacterial Action of Iodine.

Strength of Solution in grains per gallon.	Colonies of Bacteria in c.c. before treatment.	Colonies of Bacteria in c.c. after treatment.	Time of contact in minutes.	Remarks.
2·8	Innumerable.	12	5	Iodine in
2·8	"	3	15	pot. iodide
2·8	1000	1	5	1 I to 3 KI.

Of the three agents examined iodine seems to be the most powerful.

Laboratory, 196, St. Vincent Street,
Glasgow.

Action of Oxygen upon Alcoholic Liquors.—It has been recently established that the "fusel" in raw spirits can be removed by the introduction of a current of pure oxygen. The flavour of the spirit is not only improved, but its physiological action is much ameliorated.

NOTICES OF BOOKS.

A Tabular Atlas of the Chemistry of the Metals. Comprising the Arrangement on a Novel Plan in Sectional and Tabular Form, devised to rapidly convey Information on the Data relating to the History, Distribution, Preparation, or Metallurgy Properties; Chemical, Medical, Pharmacal, and Technical Uses; Analysis and Toxicology of the said Metals, their Organic and Inorganic Compounds. *Metals of the Alkalies, Cesium, Rubidium, and Potassium.* By JOHN FREMONT SLEEPER.

OUR opinion of this work, judging from the specimen which has fallen into our hands, cannot be other than favourable. It is a cyclopædia of the metallic elements and their compounds, both with each other and with the non-metals.

The plan followed is apparently novel as applied to literary matter; it has been actually patented. The exact claims of the patent will be, we think, difficult to define.

The names of the substance will be found in vertical columns at the left-hand of each page, whilst in horizontal columns come in succession the preparation (or occurrence), the colour, crystalline form, &c.; the reaction (presumably with litmus), the specific gravity, the formula, the solubility in water at 15° and at 100°, in absolute alcohol, in sulphuric acid, nitric acid, hydrochloric acid, potassium hydroxide, ammonia, ammonium chloride, alkaline carbonates, acetic acid, ether; behaviour on exposure to air and light, to heat, on fusion with a number of substances, on ignition; the molecular weight, and we presume the atomic weight if an element; the percentage composition; and, lastly, miscellaneous information. The information required is to be sought at the intersection of the vertical and the horizontal column.

As an instance of the extent and accuracy of the information given, we may mention that the instructions for the quantitative analysis of potassium salts occupy some twenty pages.

We cannot help regarding the heading "proprietary preparations" (or, in plain old-fashioned language, quack nostrums) as emphatically below the dignity of such a work as that before us.

The physical and chemical characters of each metal are arranged under the headings—Equivalence; atomic volume; atomic weight; specific heat; specific gravity; colour and crystalline form; hardness; malleability; ductility; electric conductivity; refraction equivalent; permanence in air; permanence in water; on exposure to heat; action of solvents; exposure to the action of the following inorganic substances; ditto, of organic substances.

In the Prospectus we are advised to compare the specimen of the work on potassium compounds with the data given in Watts, Wurtz, and Gmelin, and note "how unsatisfactory in comparison will be the information they impart." An opinion quoted even says that the work "will elevate American scientific authorship above the level of the English and the German."

That Mr. Sleeper's *magnum opus* will be of immense value is indisputable, and we hope that it will be appreciated as it merits.

Kemp and Co.'s Prescribers' Pharmacopæia. A Synopsis of the more recent Remedials, Official and Unofficial, with a Therapeutic Index. Third Edition. Bombay: Kemp and Co., Ltd.

PENDING the avatar of the long-promised Imperial Pharmacopæia, the book before us is likely to prove of great use in India and the tropical colonies. The climatic requirements of such regions, as regards solubilities, &c., have been carefully considered. A contemporary refers to the difficulties of dispensing when the thermometer at

the dispensing counter marks 100° F. A very valuable feature is the notice of indigenous Indian drugs which may serve as substitutes for European or American products.

The chief thermometric scales are given, though that of Réaumur is now scarcely necessary. A table of hydrometer scales might have been given, so far at least as to show the comparison of Twaddell's scale with direct specific gravity. For Baumé there is no occasion.

CORRESPONDENCE.

THE SCIENCE AND ART DEPARTMENT.

To the Editor of the Chemical News.

SIR,—In one respect, at all events, your correspondent "S." is mistaken with regard to the new regulations of the Science and Art Department; I refer to that of the three stages. I entered for the elementary examination in Practical Chemistry in company with an acquaintance who was up for the Honours; we both passed. The next year I presented myself for the advanced, and he for the elementary stage (as he could not obtain his Honours certificate). This time the examiners were kind to me, but not to him. Consequently, although this happened nearly twenty years ago, my fellow candidate has nothing to show for his Honours to this day.

Possibly "payment on results" is in the first place responsible for this deplorable state of things, but by preventing a repetition of it the Department, so far from being retrograde, has made a step in advance.

That it should have been possible to pass in Honours without any knowledge of the fundamental principles of the science, is not only a disgrace to the Department, but to the nation also!—I am, &c.,

W.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 12, September 21, 1896.

This issue contains no chemical matter.

Zeitschrift für Analytische Chemie.
Vol. xxxv., Part 3.

Contributions to the Examination of Honey.—Some portions of this voluminous memoir will be inserted in full.

Further Remarks on the Quantitative Separation of the Proteid Substances present in Beer Wort.—H. Schjerner.—This paper, which is a communication from the laboratory of Neu-Carlsberg, is too extensive for insertion.

Double Compounds of Aniline with Metallic Salts.—J. L. C. Schröder van der Kelk.—The compounds of ferric salts with aniline except ferric chloride have not been prepared, and, like the latter, they are not applicable in microscopic practice. The process is perfectly useless for the detection of iron, but the reactions for cobalt and nickel are available.

Determination of Nicotin and Ammonia in Tobacco.—Dr. Viktor Vedrödi.—A reply to the objections made by Kissling to the author's process (*Zeitschr. Anal. Chem.*, xxxiv., p. 413).

New Volumetric Method of Determining Soluble Compounds of Iodine.—Prof. Dr. E. Riegler.—Already inserted.

Quantitative Determination of Zinc in Organic Salts.—Gottfried van Ritter.—The zincic salt is covered with concentrated nitric acid, the acid is cautiously evaporated off, and the residue is ignited. The zinc is left behind as oxide. The author gives instances of the accuracy of his method as applied to zinc acetate, lactate, succinate, tartrate, mucate, benzoate, and hippurate. The excess of nitric acid must be driven off at a gentle heat, to avoid spitting, and the apparently dry residue must not be at once ignited, but merely heated a little more strongly than before. These two operations can be easily and safely executed in a Lieben muffle. The residue is then heated until white. Porcelain crucibles should be used, as platinum is strongly attacked. Experiments in which sulphuric acid was used instead of nitric acid gave results too high by several per cents.

Behaviour of Nitrogenous Organic Bodies with Potassium Polysulphides at High Temperatures.—Heinrich Aufschläger.—A great number of nitrogenous substances, inorganic as well as organic, was investigated, and the transformation of nitrogen into sulphocyanogen was found to be a universal reaction of nitrogenous bodies. The field of potassium sulphocyanide is about 10 per cent of the quantity theoretically possible.

Occurrence of Iodine in Water.—Prof. Dr. Lecco.—Besides the iodiferous saline springs sea-water is generally considered the only water containing iodine. The statements found in literature concerning the presence of iodine in other waters are often discordant. In researches dating back to 40 years ago and beyond it was stated that almost every water contained iodine, as also the air, the earth, and the majority of animal and vegetable substances. Subsequent authorities have been unable to show the presence of iodine in air, water, &c. This discrepancy may be explained either by assuming that the reagents used were not always sufficiently pure or that some of the methods used for the detection of iodine are defective. The reaction for iodine with nitrous acid and carbon disulphide is so sensitive that those quantities of iodine which occur, e.g., in iodiferous salt springs, are easily detected. In mineral waters which contain per litre only 0.1 m.grm. iodine it is almost always possible to detect the iodine directly and determine it colorimetrically without previous concentration. The author then gives an account of the Belgrade drinking waters, which are chiefly bad. In the good waters it was fairly easy to recognise iodine, but of the twelve town wells examined which yield bad water traces of iodine—scarcely perceptible—were recognised in one only. Hence the question arises whether the direct recognition of iodine in water does not bear some relation to other constituents of water which possibly interfere with the ready detection of iodine in bad waters. The author's results show that iodine is more generally diffused than is ordinarily assumed. He intends to continue his experiments on the occurrence and the detection of iodine.

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F. A. ABEL, General Director, Imperial Institute, S.W., October, 1896.
WYNDHAM R. DUNSTAN, Director of the Scientific Department.

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THE DETERMINATION OF SULPHURIC ACID, OR OF BARIUM.

(A PRELIMINARY COMMUNICATION).

By JAMES EDMUNDS, M.D., F.C.S., &c.,
Medical Officer of Health and Public Analyst for St. James's,
London.

I VENTURE to submit a process by which, in about fifteen minutes, we may make an extremely close measurement of the sulphuric acid in a small quantity of any ordinary liquid—say, in 70 c.c. of a sulphuric acid.

The process is straightforward and easy, and it requires no heating. The reagents are anhydrous salts, —easily obtained in a state of extreme purity, and, in storage, undergoing no change and attracting no moisture. Their solutions are permanent.

In accuracy of measurement the process equals that of a chlorine or silver titration, if only imperfect manipulation, and errors as to the purity, strength, and measurement of the reagents be excluded.

Scheme.—The SO_3 to be measured is precipitated with barium nitrate in excess, the residual barium is precipitated with potassium chromate in excess, the residual chromate is precipitated with silver nitrate in excess. The mixture is filtered off. An aliquot part of the filtrate is titrated for its residual silver nitrate, potassium chromate being used as indicator. The total of the residual silver nitrate, deducted from the silver nitrate originally introduced, gives the equivalent of the SO_3 .

The solutions required are:—

1. Barium nitrate N/10 and N/100
2. Potassium chromate .. N/10 and N/100
3. Silver nitrate N/10 and N/100
4. Sodium chloride N/10 and N/100
5. Potassium thiocyanate .. N/100
6. Ferric sulphate N/10
7. Calcium sulphate N/100
8. Potassium sulphate .. N/10 and N/100

The ferric sulphate is made from a solution of crystals of ferrous sulphate by boiling with nitric acid to full peroxidation of the iron, then adding sulphuric acid in large excess, and boiling off residual nitric acid so as to leave a solution of pure ferric sulphate in pure sulphuric acid. The residue is made up to volume as a N/10 solution of iron in about 5 N sulphuric acid.

This ferric indicator gives no blue colour with freshly-made solution of potassium ferric cyanide; it does not bleach permanganate, and it never evolves nitrous fumes. It keeps perfectly.

The calcium sulphate is made by weighing out 0.860 of pure selenite into a standard flask, and then adding freshly-boiled distilled water to 1000 c.c. at the standard temperature. It serves for experimental work and for control in the titration of sulphuric acids.

The potassium sulphate is used for experimental work and for general control.

Process.—Seventy c.c. of the titrate* is measured out into a 200 c.c. tall glass-stoppered bottle. Ten c.c. of N/10 solution of each reagent successively is then added, —the barium first, the chromate next, the silver last,—and the mixture is shaken vigorously for one minute after the

addition of each reagent. The mixture is poured into a filter, and a bright colourless neutral filtrate runs rapidly through.

An aliquot part of the filtrate—say 20 c.c.—is measured out into a white basin, an accurately measured round volume of N/10 sodium chloride is added so as to overdo the residual silver by 0.2 to 0.5 c.c., and the solution is then distinctly yellowed by adding potassium chromate. New silver, as N/100 AgNO_3 , is now slowly dropped in, with active stirring, until silver chromate begins to redden the titrate permanently.

The chloride used, *minus* the new silver, gives the aliquot portion of the residual silver nitrate. The total residual silver, deducted from the amount of silver originally added, gives the silver shortage. The shortage of the silver is the equivalent of the SO_3 .

If the final result be not needed at once, the mixture may preferably be set aside till next day. Part of the clear supernatant solution may then be withdrawn for titration, and there is no filtering and no disturbance of volume to correct for.

If extreme precision and immediate results are needed, I filter off the mixture at once (by means of a little apparatus of my own) directly into a standard pipette or burette. In this way transference of the mixture from its tall glass-stoppered bottle is avoided, while disturbance of volume (by reason of evaporation during filtration) is entirely excluded. This little apparatus is quite simple and of great general utility, but the present crowded condition of the columns of the CHEMICAL NEWS compel me to defer its description and diagram.

In titrating attenuated sulphuric solutions, such as the London drinking waters, centinormal reagents may be substituted for the decinormal. Or, such waters may be concentrated by adding successive volumes in a boiling-down flask, and, when cold, making up to volume with freshly-boiled distilled water. After mixing, and subsidence of the CaCO_3 , an aliquot part of the clear supernatant liquid is withdrawn for titration. In technical work the routine may be modified by instituting a dosage different from the uniform 10 c.c. of each reagent. Of the solution, 70 c.c. is a convenient quantity to handle; its result expressed in m.grms. is grains per standard English gallon; one hundred sevenths of the result is m.grms. per litre. The 100 c.c. of the mixture is a convenient quantity to divide and to calculate for.

Strong sulphuric solutions should be attenuated for titration to about centinormal strength.

It will be seen that each precipitate is thrown out in the presence of an ample excess of its precipitant. This excludes the influence of any neutral zone.

A minute quantity of silver chromate would remain in solution in a filtrate charged with certain salts. Such silver chromate is compensated for exactly by using the potassium chromate indicator in the titration of the residual silver. Mohr's beautiful indicator in this case has its one defect converted into a special excellence.

The Titrate.—In some cases the titrate will need preliminary examination and preparation with a view to eliminate or to allow for interferent substances.

1. Phosphoric and other acids which would precipitate barium otherwise than as sulphate, should be eliminated by shaking with milk of pure lime in slight excess, boiling, passing in carbon dioxide, boiling, filtering, and washing the precipitate. This procedure would also eliminate ammonia and magnesia.

2. Lead, sulphur compounds, and other substances which would precipitate or reduce chromic acid must be eliminated.

3. Haloid radicles, and other precipitants of silver, are best measured in a preliminary volume of the solution, and ultimately deducted from the shortage of silver as calculated from the final titration. A preliminary volume of the solution is shaken with a measured volume of N/10 silver nitrate in excess, the precipitate is filtered

* The term titrate is used to indicate a liquid in course of titration.

off and the filter washed, and the residual silver is then titrated by means of thiocyanate with ferric sulphate.

4. Carbonic acid may be boiled off if necessary. The solution, if not neutral, must be carefully neutralised by means of N/10 soda or acetic acid. Any alterations in volume which supervene in preparing the solution, or in filtering off the titrate, must be redressed or taken into account.

In determining barium, 70 c.c. of its solution is shaken with 10 c.c. of N/10 solution of K_2SO_4 . The residual SO_3 is then determined by the procedure above described. The 70 c.c. must contain less barium than is equivalent to the SO_3 in the 10 c.c. of K_2SO_4 , and it must be free from substances—such as strontium or lead—which would precipitate SO_3 otherwise than as $BaSO_4$.

29, Dover Street, Piccadilly,
October 2, 1896.

LIMITING THE EXPLOSIVE PROPORTIONS OF ACETYLENE, AND DETECTING AND MEASURING THE GAS IN THE AIR.*

By Professor FRANK CLOWES, D.Sc.,
University College, Nottingham.

THE value of acetylene as an illuminant, and the discovery of its ready production from calcium carbide, have led to the manufacture of this gas in some quantity; and acetylene will probably be dealt with in still larger volume in the near future. It becomes, therefore, important to devise methods of detecting its presence in the air, arising from leakage and escape, and to measure the percentage of the gas present at any place. It is also important to ascertain what proportions of the gas, when present in mixture with air, will lead to explosion if the mixture should be kindled.

The detection of small proportions of the gas will not be readily effected by its smell when it is prepared in a state of purity. At present the smell is made much more pronounced by the impurities which the commercial gas contains. Further, the smell will not in any case furnish a means of measuring the proportion present in the air. The method applied by the writer to the detection and measurement of fire-damp and coal-gas in the air, however, serves for detecting and measuring acetylene as well. A small hydrogen flame, set to either 5 or 10 m.m. in height, as may be necessary, shows a pale but well-defined "cap" in air containing any proportion of acetylene less than the lowest explosive proportion. When the hydrogen flame is exposed to the air to be tested for acetylene in a darkened space, it is at once tinged yellowish-green. The bluish pale cap has the following heights with varying proportions of acetylene, when the hydrogen flame is 10 m.m. in height:—

0.25 per cent gives 17 m.m. cap.	
0.50 " " 19 " "	
1.00 " " 28 " "	
2.00 " " 48 " "	

When the hydrogen flame is reduced to 5 m.m. —

2.50 per cent. gives 56 m.m. cap.	
2.75 " " 79 " "	

A convenient portable form of apparatus was shown by the writer, which enabled air to be passed readily over the standard hydrogen flame in a darkened vessel, and which quickly furnished the reading of the height of the cap.

In determining the limits of explosibility, when acetylene is mixed in gradually increasing proportion with air and kindled, the writer adopted a simple method, referred to at the last meeting of the Association. It was found

that air must contain at least 3 per cent of acetylene before it can be kindled by a flame and the mixture caused to burn throughout. As the proportion of acetylene is increased, the explosive character is augmented. When 22 per cent of acetylene is present, carbon begins to separate during the burning. The amount of carbon which separates increases until the explosive character of the mixture disappears. This point is reached when 82 per cent of acetylene is present in the air.

The limiting percentages in air which are explosive are accordingly as follows, and may be compared with those already determined by the writer for other combustible gases:—

Acetylene	3 to 82
Hydrogen	5 " 72
Carbon monoxide	13 " 75
Ethylene	4 " 22
Methane	5 " 13

It will be seen that acetylene gives a wider range of explosive proportions than any other of these gases does. Probably this is due to its endothermic nature, which leads to the gas being able to generate heat by its own decomposition. Heat thus generated would undoubtedly aid in causing explosion, and would thus extend the limits of explosive mixtures.

THE DETECTION AND ESTIMATION OF CARBONIC OXIDE IN THE AIR.

By Professor FRANK CLOWES, D.Sc.,
University College, Nottingham.

CARBONIC oxide gas, when mingled with air in suitable proportion and fired, produces explosion. But a far greater danger arises from its poisonous nature when breathed. As small a proportion as 0.2 per cent in air produces poisonous symptoms on man. This gas is introduced into the air by leakage of unburnt water-gas and other gaseous fuels, amongst which ordinary coal-gas must be included. It is produced in the coal-mine by the firing of certain explosives, such as blasting powder and the nitro-cottons; also during an explosion of fire-damp, or by burning of coal or gob-fire. Hence carbonic oxide may be frequently encountered in air; and since it cannot be smelt or detected by any ordinary tests, it is important to make known recently devised methods for detecting and estimating the gas.

Dr. Haldane has brought forward a method which depends upon the change in colour produced in diluted blood when it is shaken up with the gas. This is probably the most delicate and accurate method known. But it requires some time for its performance, and good daylight is an absolute necessity.

Other methods are well known to the chemist which are not sufficiently delicate, and require to be carried out in a chemical laboratory.

The author recommends the flame-cap test as being at once quick of execution, sufficiently delicate, and also wide in its range of indications. The standard hydrogen-flame, 0.4 inch in height, gives a cap 0.5 inch in height in air containing 0.25 per cent of carbonic oxide, and the height of the cap increases as the percentage of carbonic oxide in the air becomes larger. The only drawback of the method consists in the fact that all combustible gases give flame-caps, and these are indistinguishable from that furnished by carbonic oxide. Hence the flame-cap test is only suitable when other combustible gases are known to be absent.

The test may be made by introducing into the air to be examined a hydrogen safety-lamp, such as has been now adopted in delicate tests for fire-damp and coal-gas. Since, however, there might be serious risk involved in entering and breathing the atmosphere, it is preferable to

* Abstract of a Paper read before the British Association (Section B), Liverpool Meeting, 1896.

collect a sample of the air and pass it over the flame, as is done by Mr. Redwood in testing for petroleum vapour. A still more simple plan will often consist in pumping the air to be tested over the standard hydrogen-flame in a suitable apparatus, such as was exhibited by the writer. It consists of a small metal cylinder with glass front, within which the hydrogen-flame burns, being fed from a pocket cylinder of the compressed gas. The cylinder containing the flame is mounted on a folding portable camera tripod. The air to be tested is drawn through a long rubber-tube, by working a valved rubber ball by the hand, and is made to pass over the hydrogen flame. A black cloth is thrown over the observer's head and the flame-cylinder, so as to enable the flame-cap to be accurately observed in darkness, and the height of the cap is registered by shifting a bent wire, moving stiffly in a stuffing box, until it just touches the tip of the cap. On removing the black cloth, the percentage of carbonic oxide is then at once read off upon a scale on the cylinder, the number standing opposite to the top of the movable wire. Other details of the method will be found in a book on the "Detection and Estimation of Inflammable Gases in the Air," which has been recently published for the writer by Messrs. Crosby Lockwood and Sons.

The flame-cap test applied in this way presents the advantage of being rapid and delicate, and may be applied without any risk to the operator.

ESTIMATION OF SULPHUR IN ORES.

By J. H. STANSBIE.

THE following modification of the usually described process for the estimation of sulphur in ores is found to give accurate results, and to require a much shorter time for its completion:—

About 0.5 gm. of the finely-powdered ore is weighed into a beaker, and 10 c.c. of strong nitric acid added. The acid is then raised to boiling, and the action continued until the sulphur has largely separated out and is floating on the surface of the liquid in globules. The beaker is then removed from the hot plate, and allowed to cool. When cool about 1 c.c. of bromine is added. The globules of sulphur are at once taken up by the bromine. The beaker is then gently warmed for a few minutes on the hot plate, the clock-glass removed, and the liquid evaporated just to dryness. About 5 c.c. of strong hydrochloric acid are added, and the beaker heated until the residue is completely removed from the bottom. About 100 c.c. of hot water are now added, and the contents of the beaker boiled for two or three minutes. The siliceous residue is then filtered off, and the filtrate is ready for the precipitation of the sulphate by barium chloride.

If rapid working is of importance, the whole of the operations described above may be carried out in less than an hour. The solution for the estimation of the metals present may be prepared in a similar manner.

As a check upon the method, it was worked in conjunction with another method which has been found to give good results with several sulphide ores:—

About 0.5 gm. of the finely-powdered ore is weighed in a porcelain crucible, and 3 grms. of pure lime is gradually mixed with it by stirring in a little at a time with a thin glass rod. The crucible is then placed in a moderately hot gas-muffle, and left for an hour.

The contents of the crucible are transferred to a beaker, a little water added, and then a few drops of bromine, to ensure complete oxidation of the sulphur to sulphate. The solution is heated, hydrochloric acid added (a little at a time), and the liquid boiled until all the soluble matter is dissolved. The solution is filtered from the siliceous residue, and the sulphate precipitated

from the filtrate by barium chloride. The following results were obtained.—

1.—Artificial Cuprous Sulphide.

By nitric acid and bromine... .. 20.94 per cent sulphur
By roasting with lime... .. 20.97 " "

2.—Copper Pyrites.

By nitric acid and bromine... .. 27.46 per cent sulphur
By roasting with lime... .. 27.41 " "

To prove the completeness of the oxidation of free sulphur by nitric acid and bromine, 0.1126 gm. of pure sulphur was treated with the mixture, the solution neutralised with sodium hydroxide free from sulphate, evaporated to dryness with hydrochloric acid, to get rid of nitric acid and bromine, taken up with a little hydrochloric acid and water, and the sulphate precipitated by barium chloride.

0.8198 gm. $\text{BaSO}_4 = 0.11258$ gm. sulphur was obtained.

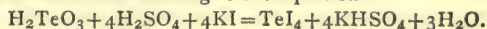
As far as the writer is aware, the powerful and extremely rapid action of a mixture of nitric acid and bromine upon free sulphur has not been noticed before, and from his experiments he is convinced that it is well worth the attention of those who are frequently dealing with sulphide ores.

Metallurgical Laboratory,
Municipal Technical School, Birmingham.

THE DETERMINATION OF TELLURIUM BY PRECIPITATION AS THE IODIDE.*

By F. A. GOOCH and W. C. MORGAN.

It was known to Berzelius that hydriodic acid and tellurous acid interact with the formation of tellurium tetraiodide, which is converted by water into an oxyiodide and by excess of an alkaline iodide into a soluble double salt. Wheeler (*Amer. Journ. Sci.*, xlv., 267) has shown that the double salt which is formed when tellurous iodide is boiled in a strong solution of potassium iodide in dilute hydriodic acid is definite, and has the constitution represented by the formula $2\text{KI} \cdot \text{TeI}_4 \cdot 2\text{H}_2\text{O}$. We have observed, however, that when potassium iodide is added to a cold solution of tellurous acid containing at least one-fourth of its volume of strong sulphuric acid, no tendency toward the formation of a double salt becomes apparent until the potassium iodide amounts to more than enough to convert all the tellurous acid present into the tetraiodide according to the equation—



The tellurium tetraiodide which is thus formed is extremely insoluble in sulphuric acid of the strength mentioned, though soluble in excess of potassium iodide, and acted upon by water with the formation of tellurium oxyiodide and hydriodic acid. It is produced at first in the condition of a finely divided dark-brown precipitate, which upon agitation of the liquid containing it gathers in curdy masses and settles, leaving the supernatant liquid clear. By taking advantage of this tendency to curd it is possible to determine without great difficulty the exact point during the gradual addition of potassium iodide when the precipitation of the tellurium iodide is complete, and we have been able to found upon this property a very simple titrimetric method for the direct determination of small amounts of tellurium.

In our test experiments we used tellurium dioxide prepared by oxidising presumably pure tellurium with nitric acid and igniting the residue at a low red heat. Weighed

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. ii., Fourth Series, October, 1896.

amounts of the oxide thus prepared were dissolved in Erlenmeyer beakers in a very little of a strong solution of potassium hydroxide, and dilute sulphuric acid was added carefully until the tellurous acid which was precipitated upon the neutralisation of the alkaline hydroxide was just re-dissolved. To this solution sulphuric acid of half-strength was added in such amount that the solution finally obtained, after adding the aqueous solution of potassium iodide subsequently, should still contain at least one-fourth of its volume of strong sulphuric acid. The Erlenmeyer beaker was placed upon a pane of window glass supported upon strips of wood about 1 c.m. above the level of the work table, which was covered with white paper. A solution of approximately decinormal potassium iodide free from iodate, and carefully standardised in terms of iodine by a method described in a former paper from this laboratory (*Amer. Journ. Sci.*, xxxix., 188; xlv., 334), was introduced gradually from a burette into the middle of the Erlenmeyer beaker. As the drops of the potassium iodide touched the liquid the precipitation formed at the centre and travelled in rings toward the outer walls of the beaker. When the liquid became so opaque that the effect of the potassium iodide was distinguished with difficulty, the beaker was rotated and the curdled precipitate permitted to settle, and then the process of titration was continued as before. We experimented with amounts of tellurium dioxide varying from approximately 0.025 gm. to 0.1 gm., the latter quantity being as large as can be handled with accuracy without intermediate removal of the precipitate by filtration. With an Erlenmeyer beaker 10 c.m. in diameter across the bottom, and a final volume of liquid amounting to not more than 100 c.m.³, we were able to follow the precipitation most easily.

The results of a series of determinations made according to the method described and recorded in the following table are closely accordant, and in close agreement with the theory of the process if the atomic weight of the tellurium which we used is taken as 127. We feel justified in taking this number as the atomic weight of our tellurium, because the mean result of twelve oxidations by standard potassium permanganate of tellurium dioxide, prepared similarly to that which we used, and from the same lot of material, and the mean result of twelve reductions by hydrobromic acid of the telluric acid thus produced (*Amer. Journ. Sci.*, xlviii., 377 and 378), point to this figure.

Final volume, C.m. ³	Strongest H ₂ SO ₄ present, C.m. ³	Iodine value of KI used, Grm.	TeO ₂ taken, Grm.	TeO ₂ found, Grm.	Error, Grm.
50	17	0.0706	0.0223	0.0221	0.0002-
50	17	0.0764	0.0244	0.0239	0.0005-
50	17	0.1591	0.0496	0.0499	0.0003+
60	17	0.1055	0.0517	0.0519	0.0002+
60	17	0.1578	0.0498	0.0494	0.0004-
80	30	0.1591	0.0498	0.0499	0.0001+
100	30	0.3179	0.1001	0.0997	0.0004-
100	30	0.3186	0.1008	0.0999	0.0009-
100	30	0.3208	0.1011	0.1005	0.0006-
100	30	0.3208	0.1010	0.1005	0.0005-

From these results it is obvious that the method, which is very rapid, is accurate.

ON THE ESTIMATION OF CADMIUM AS THE OXIDE.*

By PHILIP E. BROWNING and LOUIS C. JONES.

IN an article entitled "The Estimation of Cadmium" (*Jour. Sci. Chem. Industry*, vol. xiii., 211), Max Muspratt discusses critically some of the methods in use for the

determination of that element. Muspratt finds that the method which involves the precipitation as carbonate, ignition and weighing as oxide, gives low results, and he accounts for these results by the well known tendency of cadmium to reduction, especially in the presence of organic matter. To avoid this reduction he dissolved the precipitated carbonate in nitric acid, evaporated to dryness on a water bath, and gently ignited the nitrate to the condition of the oxide. This treatment also gave low results, although the oxide obtained from the ignition of the nitrate was found to contain traces of sulphate from the solution of the cadmium sulphate used. A second method of treatment was to filter and dry the precipitated carbonate and remove as much of it as possible to a weighed porcelain crucible, ignite and weigh by itself. This oxide was found to be free from traces of sulphate. (Muspratt's theory is that in the ignition of the carbonate the sulphate is dissociated, while the ignition of the nitrate does not effect this result).

The remainder of the cadmium oxide adhering to the paper was dissolved in pure nitric acid, and the solution and rinsings evaporated to dryness and ignited in a weighed crucible and weighed. Here also low results were obtained which, after the extended process of manipulation, would scarcely seem surprising. If, however, Muspratt adds, the oxide obtained from the ignition of the carbonate be taken as CdO the results are satisfactory.

A third modification gives more satisfactory results. The method of treatment is the same as the last mentioned, except that the oxide obtained from the ignition of the carbonate is ignited in a stream of oxygen until no further increase in weight results.

In a former paper from this laboratory (Browning, *Amer. Journ. Sci.*, xlv., 280), one of us made use of the carbonate method for the determination of cadmium after having separated that metal from copper. The filtration was made on asbestos in a Gooch crucible, and the results were most satisfactory. The object of the work to be described is to show that when the carbonate is filtered upon an asbestos felt previously ignited the dangers of reduction are obviated, and the carbonate process is both simplified and placed among good analytical methods. The solution used for the work was one of cadmium sulphate, and the standard was determined by evaporating measured and weighed portions to dryness in the presence of a few drops of sulphuric acid, igniting at low redness, and weighing as the anhydrous sulphate. The average of several closely agreeing results was taken as the standard. Measured and weighed portions of this solution were diluted to about 300 c.m.³ with hot water and a solution of potassium carbonate, 10 per cent, added drop by drop with constant stirring until no further precipitate was obtained. The precipitate was then boiled for about fifteen minutes, when it became granular and settled quickly. It was then filtered upon asbestos, washed thoroughly, dried, and ignited at red heat until a constant weight was obtained. In several instances the weighed oxide was treated with a drop of nitric acid, again ignited and weighed, but in no case was there a perceptible change in weight. In the accompanying table the results are tabulated.

As will be noticed, the results show a plus error which might naturally be due to a slight inclusion of the alkali carbonate. To test the truth of this hypothesis, a portion of the oxide which gave a plus error of 0.0007 gm. was dissolved and tested for potassium by the perchloric acid method (Kreider, *Amer. Journ. Sci.*, xlix., 443), and an amount of that element was found equal to 0.0006 gm. of the carbonate. Another portion of the oxide which showed no error was similarly treated, and only 0.0002 gm. on the carbonate was found. The results show, as we think, that the carbonate method can be successfully applied to the quantitative estimation of cadmium without recourse to the tedious process of manipulation recommended by Muspratt.

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. ii., Fourth Series, October, 1896.

No.	CdO taken. Grm.	CdO found. Grm.	Error. Grm.
1.	0'1140	0'1143	0'0003+
2.	0'1142	0'1137	0'0005-
3.	0'1141	0'1148	0'0007+
4.	0'1141	0'1148	0'0007+
5.	0'1142	0'1146	0'0004+
6.	0'1143	0'1147	0'0004+
7.	0'1143	0'1144	0'0001+
8.	0'1139	0'1146	0'0007+
9.	0'1270	0'1272	0'0002+
10.	0'1279	0'1283	0'0004+
11.	0'1272	0'1281	0'0009+
12.	0'1278	0'1281	0'0003+
13.	0'2556	0'2561	0'0005+
14.	0'2550	0'2547	0'0003-
15.	0'1272	0'1279	0'0007+
16.	0'1281	0'1288	0'0007+
17.	0'1274	0'1278	0'0004+
18.	0'1284	0'1290	0'0006+
19.	0'1271	0'1277	0'0006+
20.	0'1278	0'1285	0'0007+
21.	0'2555	0'2555	0'0000±

GENERAL METHOD FOR THE ELECTRO-CHEMICAL PRODUCTION OF METALLIC SULPHIDES.

By RICHARD LORENZ.

IN like manner, as I have given a general method for the electro-chemical preparation of hydroxides, we may obtain the sulphur compounds of the metals; and here, also, the application of the electro-chemical method has advantages as compared with the chemical method. Whilst in the latter case we have to depend on the acid, neutral, or alkaline character of the solution, by the electro-chemical method we can precipitate any metallic sulphide from a neutral solution, if only it is insoluble in water, without the use of sulphuretted hydrogen or of a metallic sulphide.

For the performance of the experiment, we select a cathode of rod-shaped copper sulphide, and an anode of that metal whose sulphide is to be obtained. The copper sulphide is enfolded in a piece of silk, as there ensues a dissipation of the electrode during electrolysis. As electrolyte, there is used an alkaline chloride, nitrate, or sulphate.

The following experiments may be performed:—

Copper as anode, with a cathode of copper sulphide, yields a black precipitate of copper sulphide in a solution of potassium nitrate or chloride.

In the same manner, silver yields in a solution of potassium nitrate a black deposit of silver sulphide. Cadmium forms a yellow deposit of cadmium sulphide.

Tin, in opposition to its electro-chemical precipitation as hydroxide, yields here always the sulphide.

Lead, if precipitated from a solution of potassium nitrate, forms black lead sulphide.

Iron yields, in a solution of potassium chloride, a black precipitate of ferrous sulphide.

Nickel as anode in a solution of potassium chloride, with a cathode of copper sulphide, yields a black deposit of sulphide.

As a matter of course, this reaction may be applied to the production of various other sulphides and will be capable of manifold extensions. In particular, the behaviour of other sulphides as cathodes will have to be considered. In particular, the development of the principle here laid down will be important as regards the electrolytic precipitation of metallic sulphides from aqueous solutions on the application of a sulphide as cathode if it proves possible to fix the ions which appear at the anode. We might thus arrive at an electrolytic method of superseding in the chemical laboratory the nuisance of hydrogen sulphide.—*Zeit. fur Anorg. Chemie*, xii., p. 442.

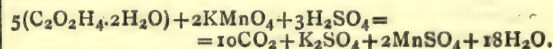
THE VALUATION AND STANDARDISING OF SOLUTION OF PERMANGANATE.

By Prof. Dr. E. RIEGLER.

THE variability of a solution of permanganate necessitates the frequent revision and determination of its value. It is very practical to possess a solution which may be kept without decomposition, and by means of which the value of a solution of permanganate can be determined at any time quickly and accurately.

I prepare such a solution by dissolving 9'9654 grms. chemically pure crystallised oxalic acid in about 500 c.c. water, adding 50 c.c. concentrated sulphuric acid, allowing the mixture to cool, and making up with distilled water to exactly 1 litre.

Each c.c. of this solution corresponds exactly to 0'005 gm. potassium permanganate, according to the equation:—



In order to determine the standard of a solution of permanganate we pour from a burette into a small flask exactly 20 c.c. of the above solution of oxalic acid, heated to ebullition, and gradually add (with agitation) from another burette, the permanganate solution in question until the last drop produces a permanent rose colouration.

As 20 c.c. of the above solution of oxalic acid correspond exactly to 100 m.grms. of potassium permanganate, we find the weight of this substance in a c.c. of the permanganate solution expressed in milligrams. Dividing 100 by the number of c.c. of this solution, which are consumed until the production of a permanent redness.

If, e.g., there were consumed 25 c.c. of a solution of permanganate, each c.c. of this solution contains $\frac{100}{25} = 4$ m.grms. KMnO_4 .

I have kept such a solution of permanganate for more than a year without the slightest change.—*Zeitschrift fur Analytische Chemie*, xxxv., p. 522.

THE REMOVAL OF SILVER AND GOLD FROM SEA-WATER BY MUNTZ METAL SHEATHING.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

(Concluded from p. 184).

(g) FROM Newcastle and Hunter River Steamship Company's upper wharf at Morpeth, N. S. Wales. Supposed to have been on piles about four years, exposed to brackish water. Very little corroded.

2000 grains gave—Silver, 5 ozs. 15 dwts. 20 grs.; Gold, 11 grs. per ton. Metallic copper, 62'5 per cent.

(h) FROM Newcastle and Hunter River Steamship Company's upper wharf at Morpeth, N. S. Wales. Supposed to have been on piles four years in brackish water. Clean, i.e., not coated with green or red scale as usual, and but slightly corroded.

2000 grains gave—Silver, 5 ozs. 7 dwts; Gold, 10'2 grs. per ton. Metallic copper, 62'4 per cent.

(i) From front of pile, No. 1 jetty (between Nos. 4 and 5 cranes), Bullock Island wharf, N. S. Wales. Submerged about twenty years in sea-water. Green, somewhat corroded, but still fairly thick and solid.

2000 grains gave—Silver, 4 ozs. 1 dwt. 16 grs.; Gold, 16'5 grs. per ton. Metallic copper, 61'6 per cent.

(j) From Circular Quay, Sydney, N. S. Wales. Submerged about forty years. The old Tank Stream, now a

* Read before the Royal Society of N. S. Wales.

sewer, has its outfall at Circular Quay, but I do not know how near to the samples of sheathing examined. Much corroded, the sheets being eaten into large holes.

4000 grains gave—Silver, 7 ozs. 19 dwts. 18 grs.; Gold, 6·5 grs. per ton.

The following were treated with sulphuric acid:—

2000 grains gave—Silver, 3 ozs. 17 dwts. 8·4 grs.; Gold, 11·90 grs. per ton.

4000 grains gave—Silver, 4 ozs. 15 dwts. 8·5 grs.; Gold, 8·62 grs. per ton.

Metallic copper, 61·6 per cent. Metallic zinc in the much corroded parts = 34·68 per cent, in the thicker parts 35·49 per cent.

The scale, extracted first with 500 c.c. of nitric acid (1—3 aq.) :—

300 grains gave—Silver, 4 ozs. 16 dwts. 11 grs.; Gold, 4 dwts. 18·5 grs. per ton.

300 grains gave—Silver, 5 ozs. 12 dwts. 19·1 grs.; Gold, 4 dwts. 18·5 grs. per ton.

300 grains gave—Silver, 7 ozs. 10 dwts. 16·5 grs.; Gold, 6 dwts. 1·8 grs. per ton.

260 grains gave—Silver, 6 ozs. 7 dwts. 4 grs.; Gold, 7 dwts. 18·6 grs. per ton.

150 grains gave—Silver, 12 ozs. 2 dwts. 18·9 grs.; Gold, 5 dwts. 15·2 grs. per ton.

150 grains gave—Silver, 7 ozs. 10 dwts. 16·8 grs.; Gold, 10 dwts. 10·8 grs. per ton.

Average, Silver, 7 ozs. 6 dwts. 18 grs.; Gold, 6 dwts. 13·9 grs. per ton.

The loose easily-removed scale of a second lot of sheathing from Circular Quay was assayed, but was first roasted and then extracted with pure sulphuric acid before scorification and cupellation. As will be seen from the results, this scale was richer in silver, the gold was very irregular, and was found to contain platinum derived from the H_2SO_4 ; hence the amounts are omitted. The H_2SO_4 had probably taken it up from the platinum stills used in concentrating it.

100 grs. gave—Silver, 25 ozs. 12 dwts. 5·12 grs. per ton.

100 " " 22 ozs. 17 dwts. 19·84 grs. "

200 " " 23 ozs. 2 dwts. 5·6 grs. "

200 " " 21 ozs. 9 dwts. 13·6 grs. "

100 " " 16 ozs. 1 dwt. 10·56 grs. "

100 " " 18 ozs. 11 dwts. 10·08 grs. "

(k) Mr. Hickson forwarded to me a supply of sheathing from the square piles of the original Queen's Wharf, Newcastle, where it had been exposed for probably thirty-five years.

The outer scale, which could be removed by a spatula, was dissolved as usual in pure nitric acid, and the residue scorified and cupelled. Two assays of 150 grains each gave—

2 ozs. 8 dwts. 18 grs. per ton of silver, but no gold.

1 oz. 3 dwts. 11 grs. " "

Then 200 grains of the hard and adherent scale under this, with scrapings of the metal itself, gave—

6 ozs. 10 dwts. 16 grs. per ton of silver.

6 ozs. 1 dwt. 12·4 grs. " "

Next the metal sheathing itself, dissolved in sulphuric acid, after removal of the above two scrapings, gave—

6 ozs. 8 dwts. 15·3 grs. of silver per ton.

7 ozs. 4 dwts. 12·4 grs. " "

The amounts of gold are omitted, since the beads were found to contain platinum.

(l) Mr. Hickson also forwarded some of the old sheathing from the bottom of the lighter *Topsy*, which was built in 1881, and had been employed at Newcastle.

Two assays were made of the scale from this, and first treated with nitric acid as usual; unfortunately there were only sufficient for 75 grains for each assay. The results obtained were—

Silver, 2 ozs. 3 dwts. 13·2 grs.; Gold, 1 dwt. 17·8 grs. per ton.

Silver, 1 oz. 5 dwts. 6·3 grs.; Gold, 20·9 grs. per ton. The metal dissolved in sulphuric acid yielded—

5 ozs. 4 dwts. 9·5 grs. silver per ton,

5 ozs. 14 dwts. 12·7 grs. "

The gold is omitted on account of its containing platinum; but an assay on 1000 grains dissolved in nitric acid gave 5 ozs. 5 dwts. 12 grs. of silver and 15·68 grains of gold per ton.

Experiments with New Muntz Metal.

Mr. Darley was also kind enough to have plates of Muntz metal placed for me on the piles of certain wharves, according to the following list, so that they might be examined from time to time, to ascertain whether they really do become richer in gold and silver; each plate was divided as shown by the accompanying diagram, the central strip, 6" × 14", was sent to me for assay, and the two other pieces, 21" × 14", were placed on a southern and northern wharf respectively, numbered and marked so that they can be readily identified when wanted for examination.

14 inches.	1 foot 9 inches.	6 inches	1 foot 9 inches.
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4 feet by 14 inches.

The assays of the new Muntz metal, before exposure to the sea-water, were made for me in the University Laboratory by Mr. S. J. Speak, A.R.S.M., Lecturer in Metallurgy and Demonstrator in Chemistry, now of Johannesburg.

They were dissolved in nitric acid (one to three parts water) free from hydrochloric acid: a few drops of hydrochloric acid were afterwards added to precipitate the silver, allowed to stand, then filtered, and the residue scorified with 500 grains of granulated lead and cupelled.

No 1. Richmond River.—Placed on back of fifth pile in middle row from eastern end of Twenty-ton Crane Wharf, south training wall, Ballina, Richmond River. Fixed 1st November, 1893; in salt water.

The assay of the new metal gave—

1000 grains gave—Silver, 5 ozs., 1 dwt. 6 grs.; Gold, 11·8 grs. per ton.

1000 grains gave—Silver, 4 ozs. 19 dwts. 11 grs.; Gold, 4 grs. per ton.

The trial sheet No. 1, after exposure at Ballina, as above, from November 11th, 1893, to September 30th, 1895, or about twenty months, gave the following results:—

Scale.—Consisted mainly of organic matter, 211 grains gave neither gold nor silver.

Metal.—Dissolved in sulphuric acid gave—

Silver, 4 ozs. 17 dwts. 19 grs. per ton; Gold contained platinum.

No. 1 a. Moruya.—Placed on the pillar pile of the crane at the town wharf, say 5 miles from the heads. Fixed 11th November, 1893; in salt water.

No. 1 a. Moruya.—The plate was taken off in October, 1896, after being exposed to the sea-water for twenty-three months, and on assaying it yielded the following results:—Four assays were made, 1000 grains being taken; two of these were first treated with sulphuric acid and the other two with nitric acid, and the residues scorified and cupelled separately.

By sulphuric acid, mean of two assays—Silver, 5 ozs., 11·5 grs.; Gold, 1 dwt. 1·8 grs. per ton.

By nitric acid, mean of two assays—Silver, 4 ozs. 8 dwts. 5·5 grs.; Gold, 1 dwt. 1 gr. per ton.

It is noticeable that the treatment with nitric acid gives a lower amount than that with sulphuric acid. The scale

from this plate (110 grains) gave no gold, and under 2 ozs. of silver per ton; but as the scale was largely organic matter, and copper oxychloride, much importance need not be attached to the percentage of silver. The inner scale from this (100 grains), treated with sulphuric acid, gave—

Silver, 9 ozs. 4 dwts., 5.76 grs. per ton; Gold contained platinum.

No. 2. Clarence River.—Placed on No. 4 pile, Yamba Wharf. Fixed 3rd November, 1893, in salt water.

No. 2 a. Shoalhaven River.—Placed on back of second pile, eastern end of public wharf, Nowra. Fixed 31st October, 1893, in brackish water. The new metal gave—1000 grains gave—Silver, 11 ozs. 6 dwts. 17 grs.; Gold, 16 grs. per ton.

(Dup.) gave—Silver, 11 ozs. 9 dwts. 8 grs.; Gold, 16 grs. per ton.

(Trip.) gave—Silver, 11 ozs. 4 dwts. 2 grs.; 16 grs. per ton.

No. 3. Macleay River.—Placed on front tier of piles at back side of pile from front of Belmore River Wharf, and on second pile on up-stream of wharf. Fixed 20th November, 1893, in brackish water.

No. 3 a. Newcastle.—Placed on No. 5 pile, from west end of Newcastle and Hunter River Steamship Company's upper wharf, Morpeth, at low water spring tides. Fixed 24th November, 1893, in salt water. The new metal gave—

1000 grains gave—Silver, 10 ozs. 10 dwts. 6 grs.; Gold, 10 grs. per ton.

(Dup.) gave—Silver, 10 ozs. 9 dwts. 5 grs.; Gold, 4 grs. per ton.

(Trip.) gave—Silver, 10 ozs. 11 dwts. 8 grs.; Gold, 8 grs. per ton.

No. 4. Richmond River.—Placed on sixth pile from eastern end of middle row of Twenty-ton Crane Wharf, south training wall, Ballina. Fixed 1st November, 1893, in salt water.

No. 4 a. Shoalhaven River.—Placed on back of second pile, eastern end of public wharf, Terrara. Fixed 31st October, 1893, in salt water. The new metal gave—1000 grains gave—Silver, 6 ozs. 3 dwts. 19 grs.; Gold, 1 dwt. 7.3 grs. per ton.

No. 5. Clarence River.—Placed on No. 3 pile, second row, Iluka Wharf. Fixed 3rd November, 1893, in salt water.

No. 5 a. Newcastle.—Placed on third front pile from end of wharf at Pilot Station, Newcastle. Fixed 30th November, 1893, in salt water. The new metal gave—1000 grains gave—Silver, 12 ozs. 18 dwts. 17 grs.; Gold, 1 dwt. 4.1 grs. per ton.

No. 6. Macleay River.—Placed on fourth pile in second tier, front of Jerseyville wharf, and on front of pile. Fixed 25th November, 1893, in brackish water.

No. 6 a. Shoalhaven River.—Placed on back of corner pile of Government Wharf, Appletree. Fixed Oct. 30th, 1893, in salt water. The new metal gave—

1000 grains gave—Silver, 10 ozs. 5 dwts. 3 grs.; Gold, 1 dwt. 7.3 grs. per ton.

No. 7. Richmond River.—Placed on second pile northern end of middle row, Low Level Wharf, Coraki. Fixed 4th November, 1893, in brackish water.

No. 7 a. Newcastle.—Placed on No. 45 pile (front) near No. 11 Hydraulic Crane, Bullock Island. Fixed 30th November, 1893, in salt water. The new metal gave—

1000 grains gave—Silver, 6 ozs. 15 dwts. 10 grs.; Gold, 1 dwt. 2.6 grs. per ton.

Plate No. 7 was taken off on September 25th, 1895, after having been exposed about twenty-three months, and examined with the following results:—

By H_2SO_4 —Silver, 5 ozs. 19 dwts. 3.8 grs.; Gold, contained platinum.

By HNO_3 —Silver, 6 ozs. 3.5 grs.; Gold, 1 dwt. 15.2 grs. per ton.

The scale (30 grains) from the plate exposed at Coraki

for twenty-three months gave 4 ozs. 13 dwts. 15.5 grains silver per ton; 2 dwts. 4.2 grs. gold per ton, but the amount available, 30 grains only, was so small that the results are of but little value.

No. 8. Newcastle.—Placed on No. 11 pile from west end of Newcastle and Hunter River Steamship Company's wharf, Morpeth, at low water spring tides. Fixed 24th November, 1893, in salt water.

No. 8 a. Moruya. Placed on an iron bark pile (sleeper) western end of Pilot's Main boat-shed at the heads. Fixed 11th November, 1893, in salt water. The new metal gave—

1000 grains gave—Silver, 6 ozs. 7 dwts. 14 grs.; Gold, 1 dwt. 2.6 grs. per ton.

No. 9. Clarence River.—Placed on No. 3 pile, Bushgrove Wharf. Fixed 3rd November, 1893, in salt water.

No. 9 a. Moruya.—Placed on centre pile of third pier of Moruya bridge, counting from Mullenderree side. Fixed 11th November, 1893, in salt water. The new metal gave—

1000 grains gave—Silver, 11 ozs. 10 dwts. 2 grs.; Gold, 1 dwt. 4.1 grs. per ton.

No. 10. Moruya.—Placed on the pile of Pilot's tide-gauge at the heads. Fixed 11th November, 1893, in salt water.

No. 10 a. Shoalhaven River.—Placed on the back of third pile from south end of wharf (front row of piles). Fixed 28th October, 1893, in salt water. The new metal gave—

1000 grains gave—Silver, 5 ozs. 18 dwts. 21 grs.; Gold, 15.6 grains per ton.

No. 11. Clarence River.—Placed on second row Lower Southgate Wharf, No. 4 pile. Fixed 3rd November, 1893, in salt water.

No. 11 a. Macleay River.—Placed on second tier of piles from face of Stuart's Point Wharf, on second pile on up-stream side, also nailed on up-stream side of pile. Fixed 18th November, 1893, in brackish water. The new metal gave—

1000 grains gave—Silver, 11 ozs. 19 dwts. 18 grs.; Gold, 1 dwt. 7.3 grs. per ton.

No. 12. Richmond River.—Placed on back of fourth pile, middle row from southern end of High Level Wharf, Coraki. Fixed 4th November, 1893, in brackish water.

No. 12 a. Macleay River.—Placed on middle pile of outside tier and on back of pile from front of Central Kempsey Wharf. Fixed 21st November, 1893, in brackish water. The new metal gave—

1000 grains gave—Silver, 11 ozs. 14 dwts. 5 grs.; Gold, 23.5 grs. per ton.

Only three of the experimental plates have been removed and assayed, viz., No. 1 Ballina, No. 1 a Moruya, and No. 7 Coraki, after an exposure of twenty-three months; the others will be left on for a longer period. In all three cases there was a loss in silver and an increase in the amount of gold.

It is unfortunate that the presence of the platinum in the otherwise pure sulphuric acid was not detected earlier, as I have not the time now to repeat the determinations of gold which had to be rejected on that account; but even without them there are perhaps sufficient assays to settle the question.

The average amounts of gold and silver obtained are—

Twelve specimens of new Muntz metal—Silver, 9 ozs. 4 dwts. 7.6 grs.; Gold, 23 grs. per ton.

Ten specimens of old Muntz metal—Silver, 4 ozs. 13 dwts. 19 grs.; Gold, 16.2 grs. per ton.

Average decrease—Silver, 4 ozs. 10 dwts. 12.6; Gold, 6.8 per ton.

It is not quite satisfactory to have to compare the assays of old specimens of metal with those of new ones, but the old specimens of Muntz metal are not likely to have originally contained less gold and silver than the new,—in fact they probably contained very much more, so that the difference is all the more striking. The assays of the metals from the *Topsy*, this second lot from the

Circular Quay and from Newcastle are omitted from the above because some of them were made with the sulphuric acid afterwards found to contain platinum.

Next the scale from the ten old sheathings gave an average of—

Silver, 5 ozs. 17 dwts. 8 grs.; Gold, 8 dwts. 1·8 grs. per ton.

Or an average increase in round numbers of over 7 dwts. of gold, and an average decrease of 4 ozs. 6 dwts. 23 grs. of silver as compared with the new Muntz metal.

The amount of gold yielded by the old metal and the scale is probably understated, since the chlorides could not be entirely removed from the old metal and they were very abundant in the scale; hence, on dissolving in nitric acid, some of the gold passed into solution as chloride and was lost.

The results do not altogether agree with the previously published views, nor with my own before I commenced the investigation. The silver has not accumulated, but on the contrary decreased; the scale, however, contains a larger amount of gold. The increase of gold in the scale may be due to the deposition of gold from the seawater on to the surface of the metal, or it may be due to the comparative non-solubility of gold in sea-water; the Muntz metal having been corroded and dissolved away, together with much of the silver, leaving the gold behind; it is probably due to both causes, *i.e.*, partly to deposition and partly to accumulation, for the superficial parts of the experimental plates Nos. 1, 1a, and 7, obtained by scraping them, show an increase in the amount of gold and a decrease in the amount of silver; the increase in the gold cannot in these cases well be due to mere accumulation, since the plates do not appear to have lost sufficient weight to materially increase the proportion of the residual gold.

Under the microscope some of the old sheathings show minute specks of what looks like filmy gold; they may be particles of bright Muntz metal, which have been deposited on the crust of oxychloride, oxide, and other compounds forming the scale, for brass is deposited electrolytically; on treatment with nitric acid they disappeared in the effervescence set up by solution or otherwise—these filmy specks are quite distinct from the points of bright Muntz metal which are seen on the old sheathing, and penetrating, as it were, the scale or crust, and I am inclined to regard them as gold.

As I have pointed out elsewhere, under certain conditions gold is thrown down from very dilute solution by the action of reducing agents, in the form of bright particles or crystals—the amount of gold in such a particle might be extremely small, for $\frac{1}{1000000}$ grain of gold leaf is visible under the microscope; a piece of corresponding size set free from gold lace would of course be far less in weight. I hope to investigate this matter further, and in the course of another two years it may be desirable to complete this series of experiments by examining the twenty-one plates which have been left on the piles for a longer exposure.

REMARKS ON THE SOLUBILITY OF SOLIDS IN GASES.

By HENRYK ARCTOWSKI.

THE conception which we form of "solutions" in general is very comprehensive.

There are solid solutions, liquid solutions, and gaseous solutions; therefore solutions of solids, liquids, and gases in solids, then of liquids in liquids, of gases and of solids in liquids, and we speak also of solutions of gases, or of vapours in gases, of liquids in gases, so that we extend the conception of solutions even to that of solids in gases.

Only liquid solutions have been closely examined;

concerning the solid and gaseous solutions we possess as yet only scanty information.

The multiplicity of the mixtures and the combinations, mechanical or chemical, which we include under general rubric of solutions is very extensive. But as we have not yet found any good data for a rational classification of solutions, we must apply the same universal name to all these so heterogeneous bodies.

This generalisation involves, however, a very great disadvantage; that is, we have become accustomed to regard totally distinct things from the same point of view, and consequently to overlook much which is worthy of attention. It is accepted as a postulate that "solutions are mixtures," and this assumption (which we may call *a credo*) serves as an initial point for considering the phenomenon of solution, and of solutions in all possible cases.

Still this generalisation offers great advantages, for it leads us to seek analogies where apparently only differences are present. It compels us, *e.g.*, to examine one and the same property (or one and the same series of properties), in the three different states of matter which must necessarily lead us to more general comparisons.

Let us take an example. Since the masterly researches of Gay-Lussac on solubility we have not ceased to study quantitatively the solubility of solids, especially of salts in water, and recently we have begun to extend these investigations to other solvents. In consequence of these researches various writers (Nordenskiöld, Le Chatelier, Schröder, and others) have attempted to combine all the results obtained under a simple general law, and I believe I am not mistaken in assuming that hence has arisen the manner of explaining the phenomena of solution and saturation which has found its complete expression in the theory of Nernst. And even if this theory does not strictly agree with the facts in all possible cases, if, on the contrary, the curves of solubility corresponding to the calculated numbers form in one manner an exception, this theory has the enormous advantage over other assumptions that it compels us to think, and throws a light on the track to be followed.

But as there are exceptions, since the laws formulated by Schröder on the one hand, and by Le Chatelier on the other, and which are founded on the assumption that the solutions considered are of a purely physical nature and are correct only in a limited number of cases, we must necessarily assume either that the law is illusory, or that the above assumption is false.

But known facts compel us to presuppose that the hypothesis, according to which all solutions are of a purely physical nature, is erroneous; consequently, the question arises whether, by this fact alone, the law is correct in all possible cases after all physical constants which affect the value of the solubility have been taken into account, and after the elimination of interferences of a chemical nature?

This question cannot be considered at once. But in order in some degree to prepare for the reply, we must—before all things—give account of the nature of such interferences. To this end we must, in my opinion, in the first place turn to simple solutions, and afterwards—still proceeding from the same point of view—examine by degrees more complicated cases. The comparison of the results obtained will permit us to give account of the value and the nature of the interferences, and this will inform us whether the validity of the theory on solubility extends beyond solutions of a purely physical nature.

The "tension of solution" has its quantitative expression in the values of the (molecular) solubility; nevertheless, the curves of solubility in the complicated case of aqueous solution do not correspond at all simply to the rise of temperature (and the heat of solution), and in the case of organic solvents these curves do not seem directly comparable with those of the vapour tension.

In order better to appreciate the individual influence of the different solvents upon the values of solubility, it

seems to me indispensable to append to these determinations those of the simplest case (where the part played by the solvent is absolutely null). For this purpose I see only one means, *i.e.*, to dispense entirely with the solvent. In this case the tensions of solution are evidently given by the vapour tension; and it is exactly the values of the vapour tensions of solid bodies, whose solubility in different solvents we wish to compare, which are as yet totally wanting, the determination of which would be of the highest value for their comparative study.

The property of solids to give off vapours is analogous to their diffusibility in liquids, and therefore to their solubility. The only perceptible difference is this: that in the case just mentioned the physical condition of the matter which acts as a solvent is different, and is in all possible cases without any action upon the dissolved body, since it is a gas, and since, according to Dalton, the mols. of a gas exert neither attraction nor repulsion upon the mols. of another gas.

The sublimation of solids in gases may therefore be regarded as solution, and it is necessarily a case of purely physical solution.

But instead of perfect gases we may assume as solvents superheated vapours. We may also foresee the case of strongly compressed gases and that of liquids above their critical point. We can consequently pursue this study step by step to liquid state of matter, and thus arrive at the much more complicated case of the solutions ordinary followed.—*Zeitschrift für Anorganische Chemie*, xii., p. 473.

NOTICES OF BOOKS.

The Detection and Measurement of Inflammable Gas and Vapour in the Air. By FRANK CLOWES, D.Sc., F.I.C., Professor of Chemistry in the University College, Nottingham. With a Chapter on the *Detection and Measurement of Petroleum Vapour*, by BOVERTON REDWOOD, F.R.S.E., F.I.C., Consulting Adviser to the Corporation of London under the Petroleum Acts. London: Crosby Lockwood and Son. 1896. Small 8vo., pp. 206.

FREQUENTLY recurring accidents warn us that the rejoicings with which the original safety-lamp for the coal-miner was greeted were somewhat premature. Painful experience has shown that methane—fire-damp—is not the only volatile explosive which is to be dreaded. Prof. Galloway and Sir F. Abel have shown that finely-divided coal-dust may render air explosive in the presence of a minimum of methane—perhaps even in its entire absence. According to Abel, it is not necessary that such dust should be in itself inflammable. In proof of this opinion we may adduce the very serious explosions which have occurred in the large flour mills of Minneapolis in the absence of any inflammable body, gaseous or pulverulent. Hence, in addition to preventing the accumulation of dust in mines, coal-bunkers, &c., it is found necessary in such localities to test the air. How this is to be carried out is the main subject of Dr. Clowes in the work before us. For this purpose the chief and most generally available method is the observation of the "flame-cap." This is "a very pale conical flame surmounting and partly surrounding the upper part" of the flame of a candle or lamp placed in a mixture of air and methane. This cap varies in size and colour according to the proportion of inflammable gas present, as shown in the frontispiece. But the greatest accuracy and delicacy is attained with a hydrogen gas flame burning in a specially-contrived apparatus. The sound test and the electric test are less trustworthy, and the apparatus required is expensive and inconvenient. The hydrogen gas required for testing is introduced into the lamp in a compressed state.

The detection and measurement of carbon monoxide in

the air forms the subject of a separate chapter. The author lays a due weight on the highly poisonous character of this gas, even in small proportions. It is distinctly dangerous if present to the extent of 0.2 per cent, and at 1.3 per cent it would undoubtedly prove fatal. Dr. Haldane, who has made most valuable researches on the physiological action of this gas, recommends that a man having to enter an atmosphere suspected to contain carbonic oxide, should carry with him a mouse confined in an open wire cage. If this poisonous gas is present, the mouse will become insensible in about one-twentieth of the time necessary to produce this effect upon a man. He is of opinion that the application of this test would be perfectly legal—a point of which we are by no means certain.

The explosive properties of petroleum vapour are fully explained by Mr. Boverton Redwood, who has made this subject his own.

The work will prove highly valuable to mining engineers, owners and managers of coal mines, and to all persons connected with the storage and transport of petroleum and its products.

The Cyanide Process of Gold Extraction. A Text-book for the Use of Metallurgists and Students at Schools of Mines, &c. Second Edition, Re-written, Enlarged, and Illustrated. By JAMES PARK, Director of the Thames School of Mines, Mining Engineer, F.G.S. (Lond.), Member of the Institute of Mining and Metallurgy, late Geological Surveyor and Mining Geologist to the New Zealand Government. Authorised Text-book for N. Z. Government School of Mines. Auckland, N. Z.: Champaloup and Cooper. Melbourne: G. Robertson and Co.

THIS book is mainly devoted to an account of the McArthur-Forrest process, *i.e.*, the solution of the gold followed up by precipitation with metallic zinc. The reader is cautioned that cyanide solutions, even if very dilute, act energetically upon the copper sulphides, oxides, and carbonates, and the antimony sulphides. Hence if these substances are present, even in small proportions, the McArthur-Forrest becomes impracticable, on account of the waste of cyanide. It is also inapplicable to ores in which the gold occurs in a coarse condition. The statement of Gmelin that mercury is not acted on by cyanide is disproved by actual working in New Zealand, *e.g.*, at Waihi. Cyanide is also sometimes wasted by the presence of charcoal and partially carbonised wood. The statement that copper sulphides are not dissolved by cyanide has been fully disproved by the elaborate experiments of Prof. Skeay. Free sulphur and zinc and lead sulphides are also more or less soluble in cyanide.

We are informed that the problem for the chemist at the cyanide works is to find a practicable method whereby all the sulphur of antimonial and cuprous sulphides can be made to combine with the cyanogen rather than with the potassium of the cyanide. Manganese oxides have been known to occasion an abnormal consumption of cyanide. The strength of cyanide solution which dissolves a maximum percentage of gold depends on the character of the ore.

The zinc used for precipitating the gold should be free from arsenic and antimony, though a little lead is advantageous.

The Park-Whittaker cyanide process for cupriferous gold ores commences with chlorinisation, the soluble copper chlorides being washed out with water. An alkaline wash is then applied, and finally the gold and silver are extracted with dilute cyanide. The copper is withdrawn from the solution by treatment with scrap-iron.

Other methods for the extraction of gold, not turning on the use of cyanide, are not brought into consideration in this work.

In a concluding chapter cautions are given concerning

the highly poisonous character of the soluble cyanides. Only one fatal case, we are told, has occurred in New Zealand. Solutions of cyanide, if applied to the skin, occasion, in some persons, painful eruptions. From this inconvenience Kaffir workmen are said to be free. It is stated, on the authority of Johann Antal, an Hungarian toxicologist, that a solution of cobalt nitrate is a perfect antidote to cyanide poisoning.

The author, following English and Chinese precedent, has appended to his treatise a series of examination questions.

CORRESPONDENCE.

THE SCIENCE AND ART DEPARTMENT.

To the Editor of the Chemical News.

SIR,—The last paragraph of your correspondent "S" in your issue of the 2nd inst. (CHEM. NEWS, lxxiv., p. 174), seems particularly true as indicating what must be the dominating thought of those who dispense the annual grant made by Parliament for distribution among committees in charge of Science classes. I should like to ask why institutions receiving aid of this kind cannot be treated on the same lines as the University Colleges, which receive a lump sum without the detailed enquiries and the great expenses of inspection and examination adopted in other cases. Surely the County Council committees are to be trusted each with a lump sum, seeing that they spend as a rule several times the amount of the grant out of local funds, and sacrifice so much time, thought, and money in providing proper instruction and appliances.—I am, &c.,

C. J. WOODWARD.

Municipal Technical School, Birmingham,
October 12, 1896.

COTTON SEEDS.

To the Editor of the Chemical News.

SIR,—On page 464 of the third and last edition of Dr. Blyth's admirable work on Poisons, there occurs an article with the heading "Cotton Seeds." The article states that "cotton seeds used as an adulterant of linseed cake, &c., have caused the death of sheep and calves. Cotton seeds contain a poison of which nothing is chemically known, save that it is poisonous; it produces anæmia and cachexia in animals when given in small repeated doses. . . . If, however, the animal has eaten a large quantity of cotton seeds, then there is gastro-enteritis, as well as inflammation of the kidneys."

From the article it is not evident if the editor specifically means whole cotton seeds or cotton seed meal. If used as an adulterant for linseed cake, it evidently refers to cotton seed cake ground, or—as it is called in the United States—cotton-seed meal. The article is probably intended to refer both to whole cotton seed and cotton-seed meal. In either case there certainly must be some mistake in regard to either fresh whole cotton seed or the fresh meal made from the seeds after the extraction of a portion of their oil. Thousands of tons of whole cotton seed are fed annually to the cattle of the southern United States, and there is also an enormous quantity of the meal fed to cattle. The hulls, which are removed from the seed before the extraction of the oil, are also used in enormous amounts in the Southern United States as a feeding-stuff. Not only are cattle fed upon the meal and hulls, but mules and horses also to a limited extent. In Atlanta, Georgia, several thousand head of cattle are fattened each year with the waste cotton seed hulls from the oil mills of that city. These cattle are shipped from

Texas to Baltimore on through bills of lading, but are allowed the permission of a stop over of about two months in Georgia to be fattened with this wonderfully cheap material. The cotton seed hulls themselves do not contain enough protein for a proper nutritive ratio. The proper proportion of protein, however, is readily imparted to the cotton-seed hulls by the addition of the meal; and even with this addition of the more expensive meal, the monthly expense of feeding a large animal is only \$2.75. The writer has fed a number of Jersey cattle with whole cotton-seed, cotton-seed meal, and cotton-seed hulls without any ill-effects whatever.

Living in the midst of a section feeding enormous quantities of whole cotton-seed and its products, the writer has never yet met with any case which would bear out the supposition that there were any poisonous qualities in this material. In the United States cotton-seed meal is used very largely as an ammoniate for fertilisers, and the pomace from castor-oil beans is also largely used for the same purpose. Castor-oil beans are very poisonous to cattle, the writer having met with several cases where cattle were quickly killed by eating only a few beans which they found lying in the field. It may be possible that the cases that Dr. Blyth refers to might have occurred where the castor-oil pomace and the cotton-seed meal were mixed accidentally, or if intentionally mixed, were so mixed as for fertilising purposes, and the mixture was inadvertently used for feeding animals.—I am, &c.,

GEORGE F. PAYNE, M.D., F.C.S.

Department of Agriculture, State of Georgia,
Laboratory of State Chemist,
Atlanta, Ga., September 24, 1896.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 13, September 28, 1896.

Absorption of the Ultra-Violet Spectrum by Crystalline Substances.—V. Agafonoff.

On a Spectrum of the Kathodic Rays.—M. Birke-land.—These two papers will be inserted in full.

The Existence and the Acid Properties of Nickel Dioxide, Barium Dinickelate.—E. Dufau.—Manganese, cobalt, and nickel all form binoxides having acid functions, yielding with the basic oxides salts whose stability decreases progressively from the manganites to the nickelites.

Researches on the Double Bromides.—Raoul Varet.—A thermo-chemical paper.

Immunity conferred by some Anti-coagulating Substances; Excitement of Phagocytosis; Increase of the Bactericidal Power of the Blood.—MM. Bosc and Delezenne.—Certain substances, such as the extract of leeches and peptone, if injected into the blood, increase the defensive power of the organism against infections.

Zeitschrift für Analytische Chemie.
Vol. xxxv., Part 3.

Examination of Red Wines for Foreign Colouring Matters.—Albin Belar.—A series of coal-tar pigments can be very simply recognised in red wines by means of nitrobenzol. Most of the coal-tar colours dissolve readily in nitrobenzol, whilst the blue or red pigment of plants—anthakyan—and the similar colouring matter of red wine are absolutely insoluble in nitrobenzol. The detection is effected as follows:—To 5 c.c. of red wine

about an equal quantity of pure nitrobenzol is added in a test-glass. The contents are at first gently shaken; in presence of magenta the nitrobenzol takes at once a bright red colour. If the nitrobenzol remains unaltered, the mixture is shaken more strongly. To remove the emulsion, the mixture is gently heated, when the emulsion disappears. The nitrobenzol collected at the bottom of the test-tube becomes, for some time, perfectly clear and permits of the recognition of the smallest traces of any magenta which may be present. After some trials, it becomes possible to recognise any magenta in the single drops of nitrobenzol which adhere to the sides of the tube after shaking. By using suitable quantities of nitrobenzol, all the magenta can be withdrawn from the red wine, so that a quantitative colorimetric determination can be effected by means of this solvent. A series of other pigments were examined by the same method as to their behaviour with nitrobenzol. The experiments were made first with watery, then with alcoholic solutions, and afterwards Istrian and Dalmatian red wines were mixed with small quantities of the following pigments. The results were alike in each case. From a watery solution of methylen blue, nitrobenzol takes up a part of the colouring matter. The nitrobenzol takes an emerald-green colour. The following pigments are dissolved by nitrobenzol without change of colour:—Magenta, purpurine (alcoholic solution), and safranin (alcoholic solution). Eosin dissolves with a vinous red, and the solution in nitrobenzol displays no fluorescence. The aqueous part, not dissolved in nitrobenzol, appears yellowish. In rosolic acid, the residual aqueous part, insoluble in nitrobenzol, has a yellow colour. Extract of indigo (sodium disulphindigotate) is quite insoluble in nitrobenzol, and behaves exactly like anthokyan (the blue colouring matter of plants). The experiments on the interesting behaviour of nitrobenzol with various colouring matters are being continued.

New Bunsen Burner.—Dr. K. Dierbach.—The construction of the new burner cannot be made intelligible without the three accompanying figures.

Determination of Phenol in Soaps and Disinfective Preparations.—H. H. Fresenius and C. J. S. Maken.—The determination of phenol in pure aqueous solutions can be easily effected by Koppeschaar's volumetric method, and its estimation in crude carbolic acid by Tóth's modification of the method of Koppeschaar present no difficulties. Its determination in soaps and disinfectants is in some cases attended with considerable difficulties. Among the methods hitherto applied, that proposed by Charles Lowe (Allen's "Commercial Organic Analysis") is worthy of notice. A weighed quantity of the soap is dissolved in hot water, and hydrochloric acid is then added until it predominates. The fatty acid set free is then filtered off. The phenol is determined in the filtrate either gravimetrically as tribrom-phenol, or volumetrically according to Koppeschaar or Tóth. From the experiments quoted, it appears that the proportion of phenol in disinfectants can be determined relatively expeditiously, and with an accuracy sufficient for practical purposes.

Volumetric Determination of Hydroxides and Carbonates, as well as of Mono- and Bi-carbonates of Alkalis, Alkaline Earths, and Magnesia.—C. Kippenberger (*Zeit. Angew. Chemie*).—Already inserted.

Sources of Error in Alkalimetry.—Fr. Scheiding (*Zeit. f. Angewandte Chemie*).—Already noticed.

Vacuum Water-bath for Temperatures above 100°.—J. Baumann and W. Horn.—From the CHEM. NEWS.

Production of Small Quantities of Ice for Laboratory Use.—H. N. Warren.—From the CHEM. NEWS.

Potassium Binodate as Ultimate Standard of most extensive Applicability.—C. Meinecke (*Chem. Zeitung*).—This salt, first proposed by C. von Thon, is met with in trade in a state of extreme purity.

Borax as an Ultimate Standard for Acids, with Methyl-orange as Indicator.—C. P. Perman and W. John.—CHEMICAL NEWS.

Aluminium Amalgam.—H. Wislicenus and H. Kaufmann.—This neutral reduction agent is very serviceable for the dehydration of alcohol, ether, &c., as it reacts for water with a formation of hydrogen and aluminium hydroxide. Aromatic nitro-compounds are reduced to amines, or, if the reaction is moderated, to substituted hydroxylamines, sodium nitrite to hydroxylamine, and even to ammonia, &c. In preparing the reagent, aluminium turnings, freed from oil, are treated with soda-lye until a strong escape of hydrogen occurs; the surface is then rinsed with water and treated for two minutes with a $\frac{1}{2}$ per cent solution of sublimate. These operations are repeated after a short time; the preparation is then quickly washed with water, alcohol, and ether, and the product kept under petroleum ether.—*Berichte*.

Detection of Small Quantities of Potassium Iodate in Potassium Iodide.—Spica (*Gazzetta Chimica*).—The author's process depends on the sparing solubility of barium iodate and its solubility in hot concentrated hydrochloric acid, from which it can be separated by the addition of water. In this manner 0.002 per cent of potassium iodate can be detected.

Oxidising Properties of Water Distilled in Copper Vessels.—Fr. Eschbaum (*Deutsch. Med. Wochenschrift*).—Such water, if mixed with normal red blood, shows the spectrum of methæmoglobine.

Determination of Sugars.—W. Fresenius and P. Dobriner.—This paper, with its accompanying tables, does not admit either of abstraction or insertion.

Examination of, and Decision on, Wines.—W. Fresenius and L. Grünhut.—The same remark must apply to this extensive memoir.

Measurement of High Temperatures, especially of the Melting Points of some Inorganic Salts.—John McCrae (*Annalen der Physik und Chemie*).—The author makes use of a thermo-element of platinum and platinum-rhodium consisting of two wires of 10 c.m. long and 0.2 m.m. in thickness. These were soldered together in the flame of detonating gas, and were melted to copper wires at their other end. The copper wires lead to a Quincke multiplier. The electromotive power of the element, corresponding to which a current is generated if the point of contact of the platinum and platinum rhodium wire is heated, and the point of junction with the copper is kept at a constant temperature, is between 300° and 1400° C. proportional to the temperature.

Contributions to a Knowledge of the Rancidification of Fats.—Ed. Spaeth.—The author sums up the results of his experiments as follows:—I. In the rancidification of fats (hog's lard), which must be regarded as a process of oxidation chiefly occasioned by the action of light and of atmospheric oxygen, the unsaturated body acids (oleic acid) are chiefly attacked with the formation of acids with a low percentage of carbon. There is also a formation of aldehydic bodies and of oxy-latty acids. II. With the progress of oxidation and the formation of free acids the volatile acids undergo a very great increment. III. All the acids participate in the formation of the free fatty acids. IV. With the increasing oxidation of the fats, their absorptive power, as well as the iodine number, undergoes a corresponding decrease, which diminution is effected by an oxidation and decomposition of the non-saturated fatty acids and by their polymerisation. Such oxidised fats exhibit in the refractometer a decidedly higher deflection than do normal fats. The increase in the deflection is decidedly due to polymerisation of the non-saturated fatty acids. V. Fats which have become rancid have in general a higher melting-point than recent fats.—*Zeit. Anal. Chem.*

MISCELLANEOUS.

Messrs. Perken, Son, and Rayment announce that their lease of the premises of their Oxford Street branch having lapsed by effluxion of time, that all business will be transacted from their headquarters, 99, Hatton Garden, Holborn Viaduct, E.C.

Farewell Banquet to J. C. Bose.—According to the *Indian Pharmacologist*, a farewell banquet has been given to J. C. Bose, Sc.D., at Bombay, in recognition of his splendid discoveries in electro-chemistry. He is about to visit the laboratories of Britain and the Continent with a view to the enlargement of the laboratory of the Presidency.

University of Aberdeen.—Mr. James Hendrick, B.Sc., F.I.C., Lecturer on Agricultural Chemistry, will deliver his Inaugural Lecture, in Marischal College Buildings, on Friday, 23rd current, at 3 o'clock p.m. Subject: "The Relations of Science to Agriculture." All interested are invited. Those proposing to attend any of the courses may now communicate with Mr. Wilson or Mr. Hendrick.

The British Flint-glass Trade.—It is announced that this country has lost nine-tenths of this important and—until of late—flourishing manufacture. The *Chem. Zeitung* ascribes this disaster in great part to the exertions of the trades' union, which still continues to fight literally against its own bread and butter.

Trades' Unionist Demands.—The recent Congress of Trades' Unions have adopted the following marvellous resolution:—"That this Congress condemns the practice of some railway companies in subjecting their men to scientific tests (for colour-blindness) at the hands of officials incompetent to apply them, instead of practical tests with day- and night-signals. It therefore requests the Committee to approach the Board of Trade with the view of securing the appointment of duly qualified persons to test the accuracy of the men's vision."

ERRATUM.—P. 177, col. 1, line 8 from bottom, for "presence" read "passage."

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1926.

THE ACCURATE DETERMINATION OF OXYGEN BY ABSORPTION WITH ALKALINE PYROGALLOL SOLUTION.*

By Professor FRANK CLOWES, D.Sc. (Lond.).

It was found repeatedly in my laboratory that during the absorption of oxygen from the Brin gas a considerable volume of carbon monoxide was evolved, although this did not occur in absorbing oxygen from the air. If the evolution of the gas was known to take place, and carbon monoxide was subsequently absorbed by cuprous chloride solution before reading off the residual nitrogen, the estimation of the volume of oxygen was correct; if this precaution was not taken, the estimation was open to serious error. Repeated trials with varying proportions of pyrogallol and potassium hydrate showed that the evolution of carbon monoxide might be entirely prevented by using a sufficiently large excess of potassium hydrate. With the following proportions no fear of this source of error need be felt, even when pure oxygen is being absorbed:—160 grms. of potassium hydrate and 10 grms. of pyrogallol in 200 c.c. of solution. This solution is prepared by dissolving 160 grms. of potassium hydrate in 130 c.c. of water, and then dissolving the 10 grms. of pyrogallol in the alkaline solution.

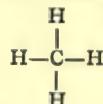
CONSTITUTION OF THE MOLECULE.

By WILLIAM LONGSHAW.

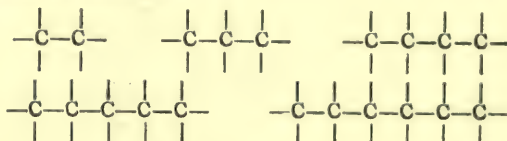
THE object of this article is to attempt to show that in organic chemistry the constitution of the molecule ought to be discussed, from the commencement, by means of spatial representations. The plan adopted by most writers is to start with uniplanar representations; then, after a considerable time, to introduce—when forced by repeated want of agreement between experimental fact and uniplanar representations—van't Hoff's theory. Moreover, they only adopt it to explain the reactions of compounds whose properties cannot be predicted by ordinary formulæ, and afterwards return to uniplanar representations. That this procedure lays these writers open to the charge of inconsistency is obvious; for if spatial representations must be employed in attempting to exhibit the reactions of substances which contain so-called asymmetrical carbon atoms, &c., it follows that they should be employed consistently throughout the discussion of the constitution of the molecule.

The view of a molecule in terms of the molecular theory, gives great support to the above contention. A molecule consists of a number of atoms which move about together. Since atoms are, by the assumptions of the molecular theory, small particles of matter, these, in the molecule, must be arranged in space. Further, the properties of matter compel us to infer that the atoms in the molecule are undergoing certain movements besides those due to the movements of the molecule as a whole. At any particular temperature these movements have a certain intensity; they decrease with the temperature, and at absolute zero they cease to exist. From the above, it follows that any representations which attempt to summarise the properties of substances ought to involve the positions of the atoms in space and their movements.

By examining the origin, mode of development, and uses of uniplanar representations, many reasons are rendered evident why they should be discarded. They have their origin in the fact that one atom of carbon combines with four atoms of a monad element. This fact is graphically illustrated by a representation, as shown—



From this fundamental conception has been developed—by methods which have never been explained or justified—other representations, and the following may be taken as skeletons:—

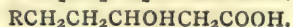
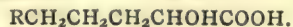


These are the class of "pictures" which figure so conspicuously in the discussion of the constitution of the molecule in our text-books. Therefore, we must point out that ordinary formulæ are excessively vague and indefinite. It has been well said, "that vagueness and incapability of precise proof—or disproof—often enable a false theory to live, and that with those who love truth vagueness should excite suspicion."

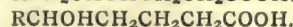
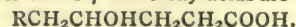
Uniplanar representations are employed to predict the number of isomers. When we remember that they fail to do so—(1) when the molecule contains one or more asymmetrical carbon atoms, (2) when the molecule contains a double bond, and other conditions, (3) in the ring compounds, &c., &c.—we must ask by what right are these formulæ employed for this purpose.

From the above, it follows that we cannot employ definite language when discussing ordinary formulæ—undoubtedly a very grave objection to their employment. This fact does not seem to be recognised by some writers. For example, Messrs. Perkin and Kipping, in their "Organic Chemistry," p. 55, say:—"They [viz., ordinary formulæ] express, in fact, in a concise and simple manner the most important chemical properties of the compound." This statement, unfortunately the most important in the book, is not in accordance with fact. This is greatly to be regretted, as it will find its way into the hands of many young students. For, in the first place, ordinary formulæ fail to account for the numbers of isomers known, and therefore they cannot express the reactions of these and allied substances. The above applies to a very large number of compounds.

Not only, however, do ordinary formulæ fail to express the reactions of many compounds, but in some cases they absolutely predict reactions which will not take place which are known to occur. An example of this is afforded by the oxy-acids. The α and β oxy-acids do not form a lactone. Their formulæ are—



The formulæ of the γ and δ oxy-acids are—



If we attempt to infer from the latter formulæ whether they will form a lactone, bearing in mind the experience gained from the α and β oxy-acids, we come to the conclusion they will not. But this conclusion is directly opposed to experimental fact. Almost any number of similar examples can be quoted—so-called straight chain compounds containing four and five atoms of carbon affording the most.

Now, then, let us sum up the objections to the use of

* Read before the British Association (Section B), Liverpool Meeting, 1896.

uniplanar representations in the discussion of the constitution of the molecule.

1. They do not take into account the spatial relations of the atoms nor their movements.

2. They are extremely vague.

3. The number of isomers predicted by their means does not, in many cases, agree with fact.

4. They, therefore, cannot express the reactions of many substances.

5. In some cases they predict that certain reactions—which experiment has shown to take place—will not occur.

Surely uniplanar representations of the constitution of the molecule which have the above shortcomings ought not to occupy the prominent position which they do. Ordinary formulæ do undoubtedly throw great light on the properties of substances, and should be retained if we had nothing superior to them. Have we any theory which discusses the constitution of the molecule in a more thorough manner? In van't Hoff's theory of the position of the atoms in space we have this *desideratum*. We can say in its favour:—

1. That its aim is definite—the position of the atoms in space at the absolute zero.

2. That it predicts correctly the number of isomers.

3. It gives far better summaries of the reactions of substances than ordinary formulæ—see particularly the oxy-acids, compounds containing five and six atoms of carbon, &c., &c.

We can say against it:—

1. It makes no attempt to take into account the movements of the atoms.

2. That its fundamental conception is somewhat vague, and the assumptions involved in its development are undoubtedly not in complete accordance with fact, although sufficiently near the truth to explain the facts which our incomplete experimental inquiry has brought to light. Associated as it is with these important objections, it is in every particular superior to ordinary formulæ.

The above remarks seem to lead to the contention advanced at the commencement of this article, namely, that uniplanar representations ought to disappear from text-books on Organic Chemistry, and spatial representation should be used consistently throughout the discussion of the constitution of the molecule.

BISMUTH OXY-IODIDE.

By T. R. BLYTH.

WHEN distilling the double iodide of methylamine and bismuth, $(\text{CH}_3\text{NH}_2\text{HI})_3(\text{BiI}_3)_2$, with caustic soda, in order to obtain the methylamine, the residue after distillation was almost white—a fact which could not be understood, as the ordinary subiodide (BiOI) was expected.

On analysis, the compound was found to have the composition $\text{Bi}_{17}\text{I}_{32}\text{O}_{24}$, or $\text{BiI}_3.8\text{Bi}_2\text{O}_3$, or $3\text{BiOI}.7\text{Bi}_2\text{O}_3$. As this was thought to be a new compound, some bismuth sub-iodide (BiOI) was boiled with caustic soda; the red colour soon changed to a very slight brown, resulting in the same above compound.

No account has been made of this body before; in fact, Wurtz says that caustic alkalis and weak carbonates have no action on BiOI . Two other rather complex oxy-iodides of bismuth are mentioned, namely:—

1. Wurtz = $\text{Bi}_{14}\text{O}_{15}\text{I}_{12}$ may be $4\text{BiI}_3.5\text{Bi}_2\text{O}_3$.

2. Watts = $\text{BiI}_3.5\text{Bi}_2\text{O}_3$, or $3\text{BiOI}.4\text{Bi}_2\text{O}_3$, or $\text{Bi}_{11}\text{O}_{15}\text{I}_9$.

This new body ($\text{Bi}_{17}\text{I}_{32}\text{O}_{24}$) is a light microscopically crystalline powder, having a very slight brown tint, is unattacked by boiling water or alkalis, soluble in dilute hydrochloric acid; while nitric acid decomposes it, setting free iodine; sulphuretted hydrogen decomposes it into sulphide,

Analysis.

	Found.	Theoretical.
Bismuth	82.18	82.20
Iodine	8.85	8.84
Oxygen (by diff.) ..	8.97	8.95
	100.00	99.99

ON THE EXISTENCE OF SELENIUM MONOXIDE.*

By A. W. PEIRCE.

It was Berzelius's idea that the odour of decayed cabbage which is noticed when selenium is burned in air is due to the formation of a gaseous lower oxide of selenium which he called the monoxide. The same oxide is said to be formed when selenium sulphide is dissolved in an insufficient amount of aqua regia, in the distillation of a mixture of selenium and selenium dioxide, and in the action of sulphur upon selenium dioxide.

Sacc (*Annales de Chimie et de Physique*, III., xxi., 119) records his inability to obtain such an oxide, and attributes the odour which is noticed under these conditions to a trace of selenium hydride. A very minute trace of the hydride is sufficient to develop a very considerable odour, and traces of moisture may be enough to produce a perceptible odour of the hydride when the conditions are favourable to action upon the elementary selenium. When selenium burns in air, or when its sulphide is oxidised by aqua regia, moisture is inevitably present, and when selenium dioxide is reduced by sulphur or intermixed with elementary selenium its extremely hygroscopic character implies the presence of traces of water.

It has been a generally accepted opinion of late that the selenium monoxide does not exist; but more recently, in work upon certain organic compounds of selenium, Chabrière has been led to the idea that the monoxide does exist, and that it is a solid body. Chabrière states (*Ibid.*, VI., xx., 273) that when selenium is heated in air it tends to increase in weight. At 100° C. the increase is said to be inappreciable, but at 180° C. it approaches very nearly to the limit corresponding to the formation of the selenium monoxide, SeO . Further, he says that this increase in weight when the selenium is heated to 180° cannot be due to the formation of the dioxide, since that compound, if it were formed, could be seen as a crystalline deposit; or if the temperature is too high to allow it to deposit, a loss of weight would result. He is so sure of the increase that, were it not for the fact that the monoxide has not been generally recognised, he would suggest, as a possible means for the determination of selenium, to heat it to 180° and estimate it as SeO . The selenium with which Chabrière obtained these results was reduced by acting with sodium sulphite and hydrochloric acid upon the product of oxidation of certain organic compounds of selenium of the aromatic series by means of nitric acid, and filtering on glass wool. The product when dried quickly at 100° gave results in accord with his theory of the constitution of the compounds, counting the selenium dried at 100° as existing in elementary form. Thus:—

	I.	II.	III.
Se found	0.0347	0.0680	0.0406
Se by theory	0.0349	0.0678	0.0414
	0.0002—	0.0002+	0.0008—

In other analyses of the same compounds, in which the selenium was dried at 180° instead of at 100°, the

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. ii., Fourth Series, August, 1896.

weight of the selenium was so much greater as to suggest the idea that the element had oxidised to the condition of the monoxide. Thus:—

	I.	II.	III.	IV.
SeO (?) found	0.0301	0.0525	0.0523	0.0517
SeO by theory	0.0301	0.0517	0.0504	0.0498
	0.0000	0.0008+	0.0019+	0.0019+

Had Chabrie actually found that the same identical selenium determined by drying to a constant weight at 100° did actually increase in weight at 180° to a constant amount corresponding exactly to what the weight should be were the monoxide formed, the evidence of such oxidation would be good. What Chabrie did, however, was to show that when the selenium from one sample of his compound was dried at 100° and regarded as elementary selenium, the amount of it found corresponded to his theory of the composition of his compound; while to harmonise the results of analysis with the demands of the theory, when the selenium from another sample of the same preparation was heated to 180°, it became necessary to assume that the selenium had been oxidised to the condition of the monoxide. Moreover, it has been shown very recently, by Kraft and Kaschau (*Ber. d. d. Chem. Gesell.*, xxix., 428), that the composition and constitution given by Chabrie to some, at least, of his organic compounds of selenium cannot be sustained. It has seemed to be desirable, therefore, to put the question of the oxidation of selenium at 180° to the direct test.

I have dried selenium to a constant weight at 100° C., and then have heated it to 180° C. for various periods of time, and in no single case have I observed the slightest increase in weight. In the following table are the results of these experiments. In every case the selenium was taken originally as the dioxide, prepared as described in previous articles, and precipitated in some cases with sulphurous acid, in some instances with potassium iodide, dried to a constant weight at 100°, and then heated to the temperature and for the periods indicated below:—

Exp.	Se found at 100°. Grm.	Temp.	Time.	Weight. Grm.	Loss. Grm.
1.	0.0356	110°	1 hour	0.0350	0.0006
		130	1/2 "	0.0348	0.0002
2.	0.0355	110	1/2 "	0.0350	0.0005
		130	1/2 "	0.0347	0.0003
		150	1/2 "	0.0346	0.0001
3.	0.0576	180	8 1/2 hours	0.0546	0.0030
4.	0.0576	180	8 1/2 "	0.0558	0.0018
5.	0.3324	180	2 "	0.3306	0.0018
6.	0.3500	180	1 1/2 "	0.3445	0.0055
7.	0.4274	180	1 1/2 "	0.4232	0.0042

Other experiments were made for the purpose of determining if possible just how the losses occur. The selenium, collected as usual upon asbestos in a perforated crucible, was introduced into a large glass tube placed horizontally in an air-bath in such manner that the tube extended outside the bath at both sides and remained cool at the ends. A current of dry air was drawn through ignited asbestos and then through the tube containing the selenium and crucible, and passed to the suction-pump through a glass trap filled with water. A thermometer placed within the tube, and closely adjacent to the selenium, showed the temperature of the selenium as the experiment progressed. On gradually heating the bath no change was observed at first, but at 180° C. a mirror of red elementary selenium formed on the cooler portions of the tube outside the bath, but did not extend so far as the trap. At the end of the heating the crucible was weighed and the loss determined. The washings of the tube and the trap, when acidified and tested with potassium iodide, gave no indication of selenious acid, as would inevitably be the case if selenium dioxide were

formed and volatilised during the heating. The loss is due, therefore, entirely to the volatilisation of the selenium as such.

Exp.	Se found at 100°. Grm.	Temp.	Time.	Weight. Grm.	Loss. Grm.
8.	0.0706	180°	2 1/2 hours	0.0628	0.0078
9.	0.0987	180	1 1/2 "	0.0948	0.0039*
10.	0.3192	180	4 "	0.3121	0.0071
11.	0.0983	180	3 1/2 "	0.0925	0.0058
		200	2 "	0.0876	0.0049

* In current of CO₂ instead of air.

In every case, irrespective of the reducing agent employed or details of treatment, I get a loss of weight on heating selenium in air to 180°, due to the volatilisation of the selenium. If this is so, it should be possible to so arrange the apparatus that the selenium volatilised may be caught and weighed.

A drying tube with ground-in stopper was therefore sealed to a smaller tube carrying a bulb filled with ignited asbestos. The selenium was weighed and introduced upon an asbestos felt into the larger tube, and the whole was carefully weighed.

The larger tube was heated in the air-bath, while air was drawn through the tube in the direction of the bulb of asbestos, which was outside the bath and cool. Selenium volatilised as before, very evidently, as far as the asbestos in the bulb, where it was caught. On cooling and weighing the tube and contents, absolutely no change of weight was observed. This shows that no gaseous product is formed to occasion the loss, but that the decrease of weight in the former experiments was due to the volatilisation of the selenium itself.

Thus I am unable to duplicate the results of Chabrie in this matter, although I have followed his method of treatment so far as it is described. The only difference apparent is in the source of the selenium—in this work the dioxide of known purity with which much exact work has recently been done, and in Chabrie's work the oxidation product of certain organic compounds. I fail to see, however, how this difference in origin can affect the sensitiveness of the selenium with reference to the oxidising action of the air.

Having thus been unable to obtain the monoxide in the solid state, I have made some experiments upon the oxidation of selenium by heating it in mixture with the dioxide under such conditions that the existence of a gaseous product, such as Berzelius describes it to be, would be noted, even if it were formed in very small amount.

A hard glass tube of convenient size, about 2 c.m. in diameter and 65 c.m. in length, was washed and dried most carefully and sealed at one end. Through the open end were introduced 0.0247 gm. pure selenium dioxide, freshly prepared and scrupulously protected against moisture, and 0.0250 gm. powdered selenium. The open end was then drawn out in such a way that attachment could easily be made to an air-pump, and an intervening portion of the tube constricted so as to be easily sealed later. The end was attached to a mercury air-pump and the pressure reduced to 4 m.m. By applying a flame to the constricted part the tube was sealed in that condition. The tube was heated gradually in a small combustion furnace until the whole contents were vapourised, maintained in that condition some minutes, and then cooled. At every opportunity of lower temperature the selenium vapours would condense into dark metallic drops which ran into larger and larger drops, like mercury globules, seeming to separate from the dioxide vapours. This treatment was repeated six times at intervals, the contents of the tube showing each time the same phenomena of sublimation and condensation. Nothing was observable at any time to indicate chemical change in either substance, each maintaining the characteristics of its own sublimation.

Finally the air-pump was again attached, and allowed to work until the manometer registered no pressure. Upon breaking the end of the tube by pinching it inside the rubber connector, the height of the mercury column indicated the same pressure as when the tube was originally sealed. When disconnected the tube possessed not the slightest odour.

This experiment was repeated with the sole modification that the heating was not carried to a temperature so high, and this time 0.0730 grm. freshly prepared dry selenium dioxide and 0.0730 grm. powdered selenium were sealed up in the evacuated tube and heated for seven hours at 180° C., and finally for one hour at 200°. Upon breaking the tube under conditions similar to those of the previous experiment, the contents showed no pressure and possessed no odour. Obviously no gaseous product was formed under these conditions.

I have thus been unable to find evidence of the existence of selenium monoxide, either gaseous or solid, and my experience goes to show that the peculiar smell attributed by Berzelius to the monoxide is only developed, as Sacc found, when selenium is heated in presence of moisture, and that a mere trace of moisture is sufficient to produce the odour.

In conclusion I wish to express my thanks to Prof. F. A. Gooch for many valuable suggestions during this work.

ON THE REDUCTION OF VANADIC ACID BY HYDRIODIC AND HYDROBROMIC ACIDS,

AND THE VOLUMETRIC ESTIMATION OF THE SAME BY TITRATION IN ALKALINE SOLUTION WITH IODINE.*

By PHILIP E. BROWNING.

THE reduction of vanadic acid from the condition of the pentoxide to that of the tetroxide by the action of hydriodic and hydrobromic acids has been applied to the volumetric determination of vanadium. Holverscheid ("Dissertation," Berlin, 1890) has shown that when a vanadate is treated with potassium bromide and strong hydrochloric acid, and the bromine liberated on boiling is passed into a solution of potassium iodide, the iodine set free and estimated shows the reduction to have gone to the condition of the tetroxide. This method is said to yield most satisfactory results.

Friedheim in a recent paper (*Berichte d. d. Chem. Ges.*, xxviii., 2067, 1895) gives the method favourable comment, and shows also, by a carefully made series of experiments, that the pentoxide may be reduced to the tetroxide by boiling with potassium iodide and sulphuric acid, and, further, that the reduction may be carried even to the condition of the trioxide by substituting for the sulphuric acid strong hydrochloric acid.

In both of the above-mentioned methods the iodine liberated is conducted into a solution of potassium iodide and estimated in the usual manner.

In a former paper (*Zeits. f. Anorgan. Chem.*, vii., 158, 1894) I have shown that vanadic acid may be determined conveniently and rapidly by reducing it to the tetroxide by the action of tartaric acid and estimating it in the residue by direct oxidation with standard iodine after having cooled the solution and having made it alkaline with a bicarbonate. The possibility of applying this method of oxidation to the residue after the reduction with hydrobromic and hydriodic acids led to the series of experiments which it is the purpose of this paper to describe. The advantages of the treatment of the residue are

obvious, and the general method has been applied in a number of methods previously developed in this laboratory. In the first place the complicated apparatus necessary for the distillation and collection of the bromine or iodine is unnecessary, an ordinary boiling-flask or Erlenmeyer beaker being sufficient. In case the distillation process is preferred, the residue may be treated by the method to be described as a control, and the results by both processes allowed to check one another.

For the work to be described solutions of ammonium vanadate were made and standardised by evaporating measured and weighed portions in a platinum crucible to dryness, and igniting in the presence of a drop of nitric acid.

The reduction with hydriodic acid was first tried; the method in general was as follows:—Measured and weighed portions of the vanadate solution were placed in the Erlenmeyer beakers; the amounts of potassium iodide indicated in the tables added from a 10 per cent solution, and finally 10 c.m.³ of a mixture of sulphuric acid and water in equal parts. The contents of the flask was then boiled until the fumes of iodine were no longer visible and the escaping steam gave no indication of free iodine with red litmus-paper (Gooch and Mar, *Amer. Journ. Sci.*, xxxix., p. 300). This point was reached when the volume of the liquid reached about 35 c.m.³. If large amounts of potassium iodide were used the resulting colour was green, owing to the presence of iodine, dissolved in hydriodic acid, with the blue tetroxide of vanadium; if smaller amounts of the iodide were used the resulting colour was blue. The flasks were then removed from the flame, and the contents nearly neutralised by the addition of a solution of potassium or sodium hydroxide,* cooled, and the neutralisation completed with potassium bicarbonate in excess, care being taken to add a few drops of a tartaric acid solution to prevent the precipitation of the tetroxide. To the cooled solution a solution of iodine in potassium iodide was added in slight excess. This point can be quite easily determined, as the iodine is bleached rapidly if the solution is allowed to mix thoroughly as it is drawn from the burette into the flask. After the addition of a distinct excess of the iodine the flask should be closed with a cork coated with paraffin and allowed to stand about one-half hour. It will be noticed that at the end of about fifteen minutes the iodine has ceased to bleach, showing the oxidation to be complete. I have generally allowed the flasks to stand a few minutes longer to be sure of a complete oxidation. The

	VaO ₅ taken. Grm.	VaO ₅ found. Grm.	Error. Grm.	Amount KI. Grm.	Amount H ₂ SO ₄ (1.1) c.m. ³ .
1.	0.1699	0.1690	0.0009—	1	10
2.	0.1704	0.1699	0.0005—	1	10
3.	0.1706	0.1700	0.0006—	1	10
4.	0.1702	0.1692	0.0010—	1	10
5.	0.3613	0.3620	0.0007+	1.5	10
6.	0.1805	0.1803	0.0002—	1	10
7.	0.3614	0.3620	0.0006+	1.5	10
8.	0.1811	0.1814	0.0003+	1	10
9.	0.1807	0.1815	0.0008+	1	10
10.	0.3613	0.3620	0.0007+	1.5	10
11.	0.3679	0.3674	0.0005—	1.5	10
12.	0.3612	0.3608	0.0004—	1.5	10
13.	0.2893	0.2907	0.0014—	1.5	10
14.	0.3456	0.3448	0.0008—	1.5	10
15.	0.3453	0.3448	0.0005—	1.5	10
16.	0.3907	0.3912	0.0005+	2	10
17.	0.3908	0.3893	0.0015—	1	10
18.	0.3906	0.3921	0.0015+	2	10
19.	0.3909	0.3912	0.0003+	1.5	10

* The potassium or sodium hydroxide for this work must be free from alcohol, as the solution is allowed to stand with iodine after neutralisation. It was prepared by mixing potassium or sodium carbonate in proper proportions with calcium oxide and filtering off the calcium carbonate.

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. ii., Fourth Series, September, 1896.

excess of iodine is then destroyed by standard arsenious acid solution, against which the iodine has been previously standardised, starch added, and the colour brought back with a few drops of iodine. The amount of arsenious acid solution used for the bleaching of the iodine, in terms of iodine subtracted from the whole amount of iodine used, gives the amount of iodine necessary to oxidise the vanadium from the condition of tetroxide to that of pentoxide. The results are given in the table (see preceding column).

The results are on the whole satisfactory, the average error of all the determinations being less than 0.0002. It will be noticed that large amounts of potassium iodide tend to give plus errors, probably due to the tendency of the hydriodic acid to hold iodine.

The action of the hydrobromic acid was tried in exactly the same manner. It was found that when the residual volume of the liquid in the flask reached 25 c.m.³ the blue colour appeared, and the absence of free bromine was proved by holding a paper moistened with potassium iodide in the steam. If the boiling is not carried to the point indicated, where the blue colour appears, the results come low, showing incomplete reduction. The results follow in the table.

	V ₂ O ₅ taken, Grm.	V ₂ O ₅ found, Grm.	Error, Grm.	Amt. KBr. Grm.	Amount H ₂ SO ₄ (1-1) c.m. ³ .
1.	0.1890	0.1876	0.0014—	1	10
2.	0.1886	0.1886	0.0007±	2	10
3.	0.1885	0.1882	0.0003—	1	10
4.	0.1885	0.1886	0.0001+	1.5	10
5.	0.1881	0.1873	0.0008—	1.5	10
6.	0.1886	0.1882	0.0004—	2	10
7.	0.3907	0.3894	0.0013—	2	10
8.	0.3907	0.3903	0.0004—	2	10
9.	0.3907	0.3894	0.0013—	2	10
10.	0.3909	0.3889	0.0020—	2	10
11.	0.3911	0.3903	0.0008—	1.5	10
12.	0.3902	0.3900	0.0002—	2.5	10

Average error of series = 0.0007—.

ON THE INVERSION OF SUGAR BY SALTS.*

No. II.

By J. H. LONG.

In a recent paper (*Journal of the American Chemical Society*, xviii., 120) I have shown that in their behaviour with cane sugar solutions many so-called neutral salts closely resemble weak mineral acids. Salts of the heavy metals in general have the power of inverting sugar solutions, and in some cases very rapidly, especially at an elevated temperature. The same fact has been pointed out for certain salts by others, notably by Walker and Aston (*Journ. Chem. Soc.*, July, 1895), who determined the speed of inversion of four nitrates, comparing them with dilute nitric acid. This inversion is due to the hydrolysis of the salts in question, the hydrogen of the acids formed being in all cases, probably, the active catalytic agent.

In my former paper I gave some results obtained in a preliminary investigation on ferrous iodide with very strong sugar solutions, and in the present paper I shall give the results obtained with other salts, as well as more extended tests with the iodide.

Method.

In the experiments before reported I made very strong syrups, containing usually 50 grms. of sugar in 100 c.c., and to these syrups before final dilution weighed amounts of the salts were added, the volume being brought up to

100 c.c. with distilled water. In the following series of tests the amount of sugar present is much smaller, being in all cases 50 grms. in 250 c.c. of the finished solution. This solution is much stronger than is usually employed in inversion experiments, but with many of the salts dissolved weaker sugar solutions could not be well used. The ferrous salts especially require relatively large amounts of sugar to hold them in clear solution, and as many of the experiments given below were made on such salts, it was decided to employ the same weight of sugar in all cases. For each experiment, therefore, 50 grms. of pure sugar was dissolved in water in a 250 c.c. flask by aid of heat. The strong syrup was cooled, and to it was added the salt in the powdered form or dissolved in a little water. After securing a complete solution in either way, it was diluted to the mark and shaken to mix thoroughly.

The syrup so made was poured into small tubes of thin glass for inversion. These tubes held about 20 c.c., and were three-fourths filled. They were cleaned for use by boiling in hydrochloric acid and then in distilled water repeatedly. After having been employed for several series of tests it was found sufficient to soak them twenty-four hours in weak acid, and then in distilled water, rinsing thoroughly finally. After receiving the sugar solutions they were closed with perforated rubber stoppers holding each a short glass tube with capillary opening. The tubes were placed in a receptacle, which was finally immersed in the water of a thermostat holding over 20 litres. The receptacle for the tubes consists essentially of two copper discs, 25 c.m. in diameter, soldered 6 c.m. apart on a copper rod as an axis. The lower disc is furnished with fine perforations, and the upper one with larger openings to receive the tubes. The copper axis below the lower disc ends in a hardened point, resting in a socket, and is extended above to a length of 15 c.m., ending in a grooved pulley around which a belt passes. Power applied to this belt rotates the tube receptacle, which at the same time keeps the water of the thermostat in motion. The thermostat itself consists of a large copper oven covered with asbestos boards on five sides. The top has perforations for the temperature regulator, thermometer, and rotating axis of the tube receptacle. A section of the top can be quickly removed to take out tubes, but at other times should be left closed to exclude light. The capillary tubes in the stoppers closing the inversion tubes project about 2 c.m. above the water.

With the apparatus employed it was possible to maintain a constant high temperature with a little watching through ten hours. A temperature of 85° was held with variation of less than 0.1° in either direction. With many salts the rate of inversion is exceedingly slow at ordinary temperatures, in fact almost imperceptible. For convenience in working, therefore, it was found necessary to invert at a high temperature, and 85° was chosen. In a few instances a slightly higher temperature was employed, but the results obtained are not included below.

The reaction between the sugar and salt is probably in most instances analogous to that between sugar and weak acids, and the rate of inversion may therefore be expressed by the same differential equation—

$$\frac{dx}{dt} = K(A-x).$$

The integration of this for t and $x=0$, together, leads to the well known formula—

$$K = \frac{1}{t} \text{ nat. log. } \frac{A}{A-x},$$

where A represents the amount of sugar present at the beginning of the inversion, x that inverted at any time, t of an observation, and K the "constant" or "co-efficient" of inversion.

As the reaction is most easily followed by means of the polaristobrometer, A is conveniently measured by the total change in rotation which is observed between the

From the *Journal of the American Chemical Society*, xviii., No. 8, August, 1896.

beginning of the reaction and after complete inversion. α is measured by the change of rotation from the beginning up to the time, t , of any observation. For convenience common logarithms are employed in all the calculations below. As the sugar solutions were mixed with the inverting substances at a low temperature, the intervals, t , could be reckoned only from the time when the mixtures in the tubes had reached the constant temperature of the experiment. Preliminary tests were therefore made to determine several points of practical manipulation. The thermostat was first brought to a temperature of about $87-88^\circ$, and the filled experimental tubes and their receptacle immersed in it. From this a fall of temperature resulted, because of the low temperature of the solution. In five or six minutes the constant temperature of 85° was reached, and by regulation of the gas flame this was maintained. In another set of experiments it was found that the solutions in the experimental tubes could be brought to a temperature of 85° from the room temperature in four to six minutes. It appeared, therefore, that ten minutes was amply sufficient time to allow, after introducing the tubes into the thermostat, before beginning the actual observations, and this was done in all cases in the experiments given below. In the case of bodies which invert but slowly there is little objection to the loss of this first ten minutes of the reaction, but in a few instances it was found to be a decided drawback, as will be seen below.

Usually 250 c.c. of the solution was prepared for experiment, and this was filled into fifteen or sixteen tubes, and put into the thermostat. At the end of ten minutes a tube was withdrawn and cooled very quickly by immersion in cold water, or by holding it under a flowing hydrant. The contents were then poured into a polarisation tube and polarised at the constant temperature of 20° in most cases. In a few tests made in warm weather a temperature of 25° was maintained in the dark room and in the water flowing around the observation tube. This first observation gives the initial rotation, and the time of removing the tube may be put as $t=0$. Tubes were removed at different intervals following and treated in the same manner. The results of the polarisations were always very constant during the first few hours heating in the thermostat, as was found by removing and polarising the contents of three tubes, but after five or six hours less regular results were found, and I adopted the plan of taking the mean result obtained by examining two or three tubes. With fifteen or sixteen tubes I made observations at eight or nine intervals.

After polarising the liquids in the last tubes removed, the contents were mixed, returned to a tube and heated longer to obtain the end point of the reaction, that is, the point of complete inversion. The point found in this manner does not always agree with that calculated from the known weight of pure cane sugar in the original solution. Even with dilute acids the phenomenon of inversion is not as simple a thing as usually represented. As shown by Gubbe (*Ber. d. Chem. Ges.*, xviii., 2207) and others, the specific rotation of invert sugar depends not only on the concentration, but on the time, temperature, and acid used. Prolonged heating with salts produces in many cases, apparently, a slight decomposition of the levulose, from which the negative rotation of the invert sugar is found smaller than it should be theoretically. In a few instances, however, the negative rotation of the invert sugar was increased. From the experiments of Gubbe it may be calculated that 50 grms. of cane sugar in 250 c.c. would yield a solution after inversion, which in a 200 m.m. tube should show a negative rotation of -8.6° . The rotation observed in my experiments was usually about -8.3° , but an accurate determination was not always possible, as some of the solutions became slightly coloured before inversion was quite complete, and in other cases a negative rotation once observed seemed to grow slightly less on longer heating, making the exact end point somewhat uncertain. The discrepancies were not

large in any case, however, and I decided to take -8.3° as the true end point for the 200 m.m. tube, and -4.15° for the 100 m.m. tube.

With some of the salts examined the velocity coefficient, K , is practically constant, with others it increases with the time, while in still other cases it decreases.

The sugar used in all the experiments was crystallised cut loaf of high degree of purity, and selected for the purpose. With 50 grms. in 100 c.c. it yields a solution of almost perfect clearness, which can be easily polarised in a 400 m.m. tube. Weaker solutions yield, on inversion, results which agree perfectly with the theoretical requirement.

(To be continued).

ON THE ABSORPTION OF THE ULTRA-VIOLET SPECTRUM BY CRYSTALLINE SUBSTANCES.

By J. AGAFONOFF.

HAVING had in view a qualitative study rather than measurements, properly so-called, I have been able to content myself with a very simple experimental arrangement. As the source of light I took a strong induction spark striking between cadmium electrodes. A lens of quartz of a short focus collected the rays on the slit of a large spectrometer provided with achromatic lenses of quartz and fluor-spar, a prism of fluor-spar, and a small photographic camera instead of an eye-piece. A Rochon prism of quartz without Canada balsam was installed between the collimator and the prism. We obtain thus, at the focus of the spectrometer, two spectra placed one above the other, and polarised at right angles. The crystal to be studied was fixed on a vertical graduated circle quite near the slit of the collimator; it was applied against a small hole pierced in the centre of the circle and forming a diaphragm. We could thus cause the crystalline plate to rotate in its plane and modify its azimuth with reference to the principal sections of the Rochon, without the region traversed by the rays undergoing the least change.

I have studied about 130 crystalline substances. Two only—tourmaline and hæmamellic acid—have shown polychroism in the ultra-violet part of the spectrum.

In the other substances the two spectra polarised at right angles presented no appreciable difference in this region. The absorption of the ultra-violet began at the same ray for plates cut out of one and the same crystal according to different orientations. The position of the limit depended very little on the thickness of the plate within the limits (naturally very restricted, 0.5 m.m. to 1 c.m.) in which I was obliged to operate.

Isolated absorption bands in the spectrum are very rare. I have observed such only in the following salts:—

Magnesium sulphate with $7H_2O$; absorption between the rays Cd 18 and Cd 24 (Mascart's rotation).

Nickel and ammonium sulphate with $6H_2O$; absorption between 7 and 9, and between 18 and 23.

Ammonium alum; absorption between 18 and 23.

Nickel nitrate at $6H_2O$; absorption between 6 and 9.

Potassium nitrate; absorption between 12 and 17.

We recognise at once the preponderant influence exerted upon absorption by the chemical nature of the molecule. The results which we have obtained for crystals present a remarkable agreement with those which C. Miller and J. L. Soret have obtained for saline solutions. Like these authors, we find that the sulphates are very transparent; the majority transmit the entire spectrum of cadmium; only copper and didymium sulphates absorb the rays more refrangible than Cd 17 and Cd 18 respectively; thallium alum transmits as far as Cd 18 inclusively.

The chromates absorb all the ultra-violet, and, further,

the violet and the blue. In general the presence of chrome increases absorption. Thus potassium chlorate transmits as far as Cd 24, whilst the chloro-chromate, $KClO_3$, absorbs the blue, violet, and ultra-violet. Neutral potassium oxalate transmits as far as Cd 16; chromium-potassium oxalate only as far as Cd 14.

The nitrates absorb much more than the sulphates; that of aluminium from Cd 13, that of potassium from Cd 19, and that of potassium and nickel from Cd 13.

Among seventy organic crystals which I have studied, only six transmit rays more refrangible than Cd 17; tartaric acid up to Cd 18; potassium tartrate up to Cd 23; mercury cyanide up to Cd 18; erythrite up to 26. The great transparency of crystals of erythrite is quite in accordance with Miller's observations on sugars in solution. In general the limit of absorption of the ultra-violet by organic crystals lies between Cd 9 and Cd 12. Many coloured compounds absorb all the ultra-violet. The derivatives of thymoquinone are highly coloured and polychroic, and all of them entirely absorb the ultra-violet spectrum.

The strong absorption of the organic bodies seems to indicate that the more complicated chemical molecules tend to absorb more abundantly the ultra-violet rays. We may further observe that nearly all the substances which have a strong absorption crystallise badly (except the chromates); on the contrary, the substances which crystallise well are in general transparent—such as the alums, quartz, fluor-spar, the sulphates, and, among organic substances, the tartrates, citric acid, and erythrite.

This remark, however, requires to be confirmed by more numerous observations.

Hæmamellitic acid and tourmaline, as we have seen, are polychroic in the ultra-violet. I have studied the tourmalines from different localities. The two spectra separated by the Rochon prism are distinctly different if we take care to direct the tourmaline in such a manner that one of the spectra is formed by the ordinary ray, and the other by the extraordinary ray. The ordinary ray is absorbed in its visible portion and partly transmitted into the ultra-violet, whilst the inverse holds good for the extraordinary spectrum. An analogous reversal is observed with hæmamellitic acid.—*Comptes Rendus*, cxxiii., No. 13.

INDUSTRIAL ACCIDENTS IN GERMANY

FOR THE YEAR 1895.

Province East Prussia.—There were 1327 accidents, 16 of which proved fatal.

West Prussia.—1565 accidents, 10 fatal.

Potsdam.—2764 accidents, 25 fatal.

At the aniline works at Rumburg a workman died of arsenic poisoning, arsenic hydride having been evolved.

Frankfurt-on-Oder.—There were 2017 accidents, 28 of which proved fatal. At an explosives works a man died from inhaling nitrous vapours.

Berlin and Charlottenburg.—Accidents 5010, being 723 more than in the former year. Twelve fatal. One death was occasioned by inhaling vapour of carbon disulphide. At the Berlin Gas-works a man died with symptoms of heat stroke on leaving the retort-house. The number of cases of lead-poisoning in the accumulator-works was very high.

Pomerania.—2107 cases, 22 fatal. In Posen, 1509 accidents, 37 fatal, chiefly at sugar-works.

Breslau.—3254 accidents, 35 fatal. Five men were taken ill after clearing out a Glover tower, and one died. The state of health at the white-lead works is very unfavourable. At the great arsenic works there were no accidents.

Liegnitz.—20 fatal accidents.

Oppeln.—5504 accidents, or 354 more than in the previous year.

Magdeburg.—3694 accidents, 23 fatal.

Merseburg.—2011 accidents, 19 deaths. Increased precautions have been adopted in the traffic with liquid carbonic acid. A man was killed whilst thawing frozen dynamite, and two others were injured. The "paraffin itch" seems to be disappearing. No special diseases have been observed at the chrome-works.

Erfurt.—748 accidents, 8 fatal.

Slesvic.—2906 cases. Twelve soldiers died from the explosion of a torpedo-boat. At a tannery there occurred two cases of splenic fever, one of which proved fatal. At a metal-work a man died from phosphorus-necrosis.

Hanover, Stade, Osnabrück, and Aurich.—3522 accidents. A severe explosion took place at a manure-works during the extrusion of fat from leather waste. The assumed safety of glass lamps against fire is called in question.

Münster.—Accidents, 837 cases, *i.e.*, 20 per cent more than in the previous year; 38 of the accidents proved fatal.

Minden.—712 cases. An explosion took place at a glass-works; the cause doubtful. One man was killed and two severely injured.

Arnsberg.—8653 accidents, 83 of which proved fatal. At the ammonia-works at Bulmke a boiler exploded. Two men died the same night from the burns.

Cassel.—1059 cases, 9 fatal. Six cases of splenic fever occurred at a work for weaving horse-hair, one of which proved fatal. No cases of phosphoric necrosis have been announced, but two seem to have been kept secret.

Wiesbaden.—2306 cases. A workman entered an apparatus before it had been freed from poisonous gases, and was suffocated. Two workmen perished by burning in a lacquer-works, from neglect of orders. At a chemical-works anilism becomes frequent in summer during the preparations of benzene and toluene. Lead colic occurred at lead-works and at accumulator-works.

Coblentz.—796 cases as against 736 the previous year; 14 fatal.

Dusseldorf.—Accidents 13,324, deaths 61. At a blue-dye-works a man fell into a tank of chromic acid, and died in consequence. A man at another works fell into a boiling dye-pan. At a work where chrome lyes were regenerated chrome ulcers occurred in considerable number. At a chemical work where nitrobenzene was manufactured there occurred serious symptoms of disease, such as fainting, dizziness, and paralysis.

Cologne.—Cases 3648, deaths 41.

Trier.—2291 cases, deaths 27. Mischief was occasioned by the dust of Thomas and Gilchrist slags.

Aachen.—1973 cases, deaths 18. Lead diseases occurred in the metallurgical establishments.

The laws enacted to restrict the employment of young boys and girls have done more harm than good. The children are now made to work at home on very low wages.—*Chemiker Zeitung*.

THE

ACTION OF LIGHT UPON DYED COLOURS.*

DURING the past year (1895-96) the work of this Committee has been continued, and a large number of wool and silk patterns, dyed with various natural and artificial blue and green colouring matters, have been examined with respect to their power of resisting the fading action of light.

The general method of preparing the dyed patterns, and the manner of exposing them under glass, with free access of air and moisture, were the same as already adopted in previous years.

* Report of Committee, consisting of Professor T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Liverpool Meeting, 1896.

The thanks of the Committee are again due to James A. Hirst, Esq., in whose grounds the patterns were exposed at Adel, near Leeds.

Each dyed pattern was divided into six pieces, one of which was protected from the action of light, while the others were exposed for different periods of time. These "periods of exposure" were made equivalent to those adopted in previous years by exposing, along with the patterns, special series of "standards," dyed with the same colouring matters as were then selected for this purpose. The standards were allowed to fade to the same extent as those which marked off the "fading period" in previous years, before being renewed or before removing a set of dyed patterns from the action of light. The patterns exposed during the past year are therefore comparable, in respect of the amount of fading action to which they have been submitted, with the dyes already reported upon.

The patterns were all put out for exposure on July 19, 1895, certain sets being subsequently removed on the following dates:—August 12, September 3, September 20, 1895; April 1, July 9, 1896. Of these five "periods of exposure" thus marked off, periods 1, 2, 3 were equivalent to each other in fading power, whereas periods 4 and 5 were each equivalent to *four* of the first period in this respect; hence five patterns of each colour have been submitted respectively to an amount of fading equal to 1, 2, 3, 7, and 11 times that of the first "fading period" selected—viz., July 19 to August 12, 1895.

The dyed and faded patterns have been entered in pattern-card books in such a manner that they can be readily compared with each other.

The following tables give the general result of the exposure experiments made during the year 1895-96, the colours being divided, according to their behaviour towards light, into the following five classes:—Very fugitive, fugitive, moderately fast, fast, very fast.

The initial numbers refer to the order of the patterns in the pattern books. The S. and J. numbers refer to Schultz and Julius's "Tabellarische Uebersicht der künstlichen organischen Farbstoffen."

In the case of colouring matters requiring mordants, the particular mordant employed is indicated in brackets after the name of the dye-stuff.

CLASS I.—VERY FUGITIVE COLOURS. (WOOL).

Many of the colours of this class have faded so rapidly that at the end of the first "fading period" (July 19 to August 12, 1895) only a very faint colour remains, and at the end of the fifth period (one year) all traces of the original colour have disappeared, the woollen cloth being either white or of a yellowish or greyish appearance.

Triphenylmethane Colours.

Wool Book IX.

Basic Colours.—

10. Victoria Blue R. Constitution not published.
11. New Victoria Blue B. Constitution not published.
12. Victoria Blue B. Hydrochloride of phenyl-tetramethyl-triamido-diphenyl- α -naphthyl-carbinol. S. and J. 274.
13. Night Blue. Hydrochloride of *p*-tolyl-tetra-ethyl-triamido-diphenyl- α -naphthyl-carbinol. S. and J. 275.
14. Victoria Blue 4R. Hydrochloride of phenyl-pentamethyl-triamido-diphenyl- α -naphthyl-carbinol. S. and J. 276.

Safranine Colours.

Basic Colours.—

24. Neutral Blue. Phenyl-dimethyl-*p*-amido-pheno-naphthazonium chloride. S. and J. 354.

Oxazine Colours.

Acid Colours.—

9. Gallanilic Indigo PS. Sulphonated product of the action of aniline on gallocyanine-anhydride-anilide.

24. Fluorescent Blue. Ammonium salt of tetra-brom-resorufin.

Basic Colours.—

5. Capri Blue GON. Dimethyl-tolyl-ammonium-dimethyl-amido-pheno-xazine chloride.
7. Cresyl Blue 2BS. Dimethyl-tolyl-ammonium-amido-pheno-xazine chloride.
19. Nile Blue. Dimethyl-phenyl-ammonium- α -amido-naphthoxazine chloride. S. and J. 344.
20. New Methylene Blue GG. Dimethyl-phenyl-ammonium-dimethyl-amido-naphthoxazine chloride.

Thiazine Colours.

Basic Colours.—

3. Thionine Blue GO. Zinc double chloride of diethyl-dimethyl-thionine.
4. Methylene Blue B. Zinc double chloride of tetramethyl-thionine.
8. Gentianine. Hydrochloride of dimethyl-thionine.
9. New Methylene Blue N. Hydrochloride of diethyl-toluthionine.
- , Toluidine Blue. Zinc double chloride of dimethyl-tolu-thionine. S. and J. 351.

Azo Colours.

Wool Book X.

Direct Cotton Colours.—

1. Diamine Sky Blue. From diphenitidine and amido-naphthol-disulphonic H.
2. Chicago Blue 6B. Constitution not published.
3. Brilliant Benzo Blue 6B. Constitution not published.
8. Diamine Blue 6G. Constitution not published.

Notes.—Certain colours in this class—e.g., Gentianine, &c.—fade during the first period to a grey colour possessing a moderate degree of fastness. Neutral Blue is characterised by fading to a dull reddish colour. Gallanilic Indigo PS and Diamine Blue 6G, when completely faded, leave the wool of a pronounced yellow tint.

CLASS II.—FUGITIVE COLOURS. (WOOL).

The colours of this class show very marked fading at the end of the second "fading period" (August 12 to September 3, 1895), and after a year's exposure they have entirely faded, or only a tint remains.

Triphenylmethane Colours.

Wool Book IX.

Basic Colours.—

1. Turquoise Blue, Constitution not published.
2. Turquoise Blue 2B. Constitution not published.
6. Glacier Blue. Zinc double chloride of dichloro-dimethyl-diamido-ditolyl-phenyl-carbinol.

Acid Colours.—

5. Cyanol extra. Sodium salt of *m*-oxy-diethyl-diamido-phenyl-ditolyl-carbinol-disulphonic acid.

Thiazine Colours.

10. Thiocarmine. Sodium salt of diethyl-dibenzyl-thionine disulphonic acid.

Oxazine Colours.

Basic Colours.—

27. Muscarin J. Dimethyl-phenyl-*p*-ammonium- β -oxy-naphthoxazine. S. and J. 343.
28. Metamine Blue B. Dimethyl-phenyl-*p*-ammonium- β -naphthoxazine. S. and J. 342.
29. New Fast Blue H. Constitution not published.
30. New Fast Blue F. Constitution not published.

Acid Colour.—

27. Azine Blue. Constitution not published.

Safranine and Induline Colours.

Basic Colours.—

15. Basle Blue B. Dimethyl-amido-tolyl-amido-tolyl-pheno-naphthazonium chloride.

16. Diphene Blue R. An induline colour.
17. Indazine M. Tetra-methyl-diamido-diphenazine-phenyl-chloride. S. and J. 364.
26. Metaphenylene Blue B. Tetra-methyl-di-o-tolyl-diphenazonium chloride.

Natural Colouring Matters.

Acid Colours.—

1. Indigo Carmine. Sodium salt of indigotin-disulphonic acid.
2. Indigo Purple. Sodium salt of indigotin-mono-sulphonic acid.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, *Metropolis Water Act*, 1871.

London, October 8th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined all were found to be clear, bright, and well filtered.

The rainfall in the Thames Valley during the month of September has been excessive, amounting to no less than 5'47 inches. The 30 years' average rainfall for September being 2'43 inches, there is an excess of 3'04 inches. This large amount has not, however, brought up the year's supply to the normal point; the deficiency for the nine months of 1896 being still 2'93 inches.

It will be of interest to compare the chemical composition of the Thames-derived waters for this September with that for the corresponding month last year; September, 1895, having been one of the driest, and September, 1896, one of the wettest on record.

Comparison of the Averages of the Five Thames-derived Supplies for the Months of September, 1895 and 1896.

	Rainfall, Sept., 1895				0'57	
			1896			
Common Nitric	Salt.	Acid.	Hardness.	Oxygen. reqd.	Organic Carbon.	Colour.
Per	Per	Per	Per	Per	Per	Per
gall.	gall.	gall.	gall.	gall.	gall.	Br'n: Blue.
Means.	Means.	Means.	Means.	Means.	Means.	Means.
Sept,						
1895.	1'980	0'685	12'97	0'032	0'081	0'008
1896.	2'228	0'834	13'41	0'048	0'087	0'146
						10'4 : 20
						14'0 : 20

In spite of the fact that the organic impurities in a river water are likely to be much higher in a dull wet season

than in a bright dry one, the purification resulting from large storage or impounding reservoirs, combined with filtration, is so effectual that the influence of the very exceptionally wet and sunless month is scarcely to be noticed, the organic carbon, which may be regarded as the measure of organic matter present, being only increased in the third place of decimals.

The bacteriological results are shown in the following table:—

	Colonies per c.c.
Thames water, unfiltered	1331
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	40
Ditto ditto lowest	3
Ditto ditto .. (12 samples) mean	11
New River water, unfiltered	709
New River water, from the Company's clear water well	4
River Lea water, unfiltered	1642
River Lea water from the East London Company's clear water well	14

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

NOTICES OF BOOKS.

Applied Bacteriology. An Introductory Handbook for the Use of Students, Medical Officers of Health, Analysts, and others. By T. H. PEARMAIN and C. G. MOOR, M.A., Cantab., Members of the Society of Public Analysts, Associates British Institute of Public Health, &c. 8vo., pp. 360, with 8 plates and 81 figures. London: Baillière, Tindall, and Co. 1896.

In the very face of a writer who asserts in the columns of an esteemed medical contemporary that "the whole modern doctrine of bacteriology is a gigantic mistake," we must venture to pronounce this work a timely and useful contribution to our hygienic literature, and to offer to the authors our warmest congratulations.

We find here in the first place an account of the history of bacteria, and of their place in nature. It is a most fortunate circumstance that they are proved to be plants and not animals, as otherwise their study would have been denounced as "vivisection." Our knowledge of these minute beings is traced back to Anton Leuwenhoeck, of Delft, who, about 1675, constructed a microscope sufficiently powerful to demonstrate their presence in water, saliva, &c. About a century later Spallanzani discovered the method of sterilising specimens and apparatus by means of heat. In 1830 Ehrenberg made a further advance in their study, and was followed by Cohn, Schwann, and Dusch. But the illustrious Pasteur must be considered as the creator of the modern science of bacteriology. To him we owe the final disproof of the erroneous doctrine of "abiogenesis," otherwise known as spontaneous generation. Subsequently we have witnessed a series of discoveries, although very much still remains to be done and to be established beyond the reach of controversy. It must be remembered that the study of bacteria—using the word in its most general sense—does not alone concern the physician. It is of high interest in chemistry, both pure and applied. Among the startling facts here mentioned we find that the descendants of a single bacillus, if allowed to multiply unchecked, would after three days reach the weight of 7,366 tons.

The bacteria are here arranged in four main divisions: Coccaceæ, Bacteriaceæ, Leptotrichæ, and Cladotrichæ.

Another division of the bacteria turns on their vital conditions, as pointed out by Pasteur. Some, the aerobic species, require the presence of air or of compounds giving off oxygen. Others, the anaerobic forms, can grow in the entire absence of oxygen, and some, indeed, cannot tolerate its presence.

The range of temperature at which they can exist is very wide. Some can grow at 0° , whilst others can increase at 60° to 70° . For any object to be perfectly sterilised by dry heat, it must be exposed for half-an-hour at least to a temperature of 160° to 180° . In the experiments of Frosch some species were found capable of multiplication after exposure to the temperature of -87° .

Light has been proved to have an injurious effect upon bacteria. Buchner observed that the vibrio of Asiatic cholera ceased to grow after one hour's exposure to direct sunlight. Hence specialists conclude that free access of light is an important hygienic factor.

Some bacteria have been found by Freudenreich and Serotonin to have an antagonistic action upon the growth of other species. Thus *Bacillus pyogenes faetidus* prevents the growth of *Spirillum cholerae Asiaticæ*.

The bacteria of putrefaction exert in soils a most important oxidising action. Hence a soil must not be overloaded with organic matter. "The failure of the process of oxidation is well seen in a sewage farm where sewage matter has been applied too freely. Instead of large crops being obtained the reverse is found to be the case, and the land is said to be 'sewage sick.'"

In a series of chapters the authors show the part played by micro-organisms in various diseases.

Foremost comes tuberculosis, which is fully admitted to be infectious and propagated by a special *Bacillus*. It is more prevalent in cold and temperate climates than within the tropics. Milk and meat from tuberculous cows is very infective, and in the ordinary method of cooking the bacillus is not destroyed in the centre of a joint of meat of over six pounds in weight. The virulence of the bacillus is not destroyed by desiccation and preservation as a dry powder for five months. The bacillus has on *post mortem* examination been detected in 40 to 60 per cent of persons who during life had shown no symptoms of the disease. A variety of diseases are here mentioned as inducing a predisposition to phthisis.

It is here mentioned that the Jews enjoy a partial immunity from tubercular disease, and the question is raised whether this may not be possibly due to their care in avoiding diseased meat. It is very judiciously recommended that "health resorts" which are much frequented by consumptive patients should be avoided.

Leprosy is not considered to be hereditary, nor to be influenced by the use of any particular article of food, nor by climate. *E.g.*, it is still endemic in Iceland, South Africa, and the West Indies.

Concerning typhoid fever—a disease fairly evenly distributed over the world—we are warned that carbon filters have been found to be contaminated with the bacillus of this affection. It may also multiply indefinitely in pure water. Milk appears to be another vehicle for the conveyance of the disease. Hence the addition of water—often impure—to milk should be treated as a very serious offence. We have seen the addition to milk of water from a very impure road-side ditch. Dust storms in India, South Africa, and some parts of Australia is another medium for conveyance.

The transmission of malarial disease by a microbe seems to be recognised, mosquitoes and gnats effecting the inoculation. In some persons the irritation due to a gnat bite subsides and reappears after the lapse of a certain time. The remarks on diphtheria will be found well worthy of a careful perusal. Space does not allow us to extend our examination beyond pointing out that the authors clearly recognise the mischief occasioned by the repeal of the so-called "C. D." Acts.

We think this book deserves to be studied not merely by professional men, but by the members of County

Councils and all persons having to concern themselves with public health.

Chemistry for Beginners. By EDWARD HART, Ph.D., Professor of Chemistry, Lafayette College, Eastern Pennsylvania, Ex-Fellow Johns Hopkins University, Editor of the *Journal of the American Chemical Society*. Third Edition, revised and greatly enlarged. Eastern Pennsylvania: Chemical Publishing Co. 1896. Pp. 245.

WE have here a very fair specimen of a class of work which has been of late not merely abundant, but even occurring in excess. Dr. Hart's book, unlike many of its class, embraces not merely the inorganic, but also the organic compounds. The nomenclature adopted is somewhat peculiar, the names of the four halogens, F, Cl, Br, and I, are written without the final e customary on the eastern side of the Atlantic, and their compounds are curtailed in a corresponding manner, thus fluorid, chlorid, &c. We submit that the retrenchment might be usefully carried a stage further as far as the halogens are concerned, so as to write fluor, chlor, brom, &c. This would not only bring us into harmony with Continental usage, but would be found more convenient in the formation of compound terms. The final *us* in phosphorus might also be advantageously eliminated.

Some statements in this book seem little adapted for the British, or, indeed, for the European reader. Thus, there is no mention of tellurium as a product of Transylvania. The account of basic slag contains no reference to the discovery by Thomas and Gilchrist.

We doubt whether the quantity of copperas made as a by-product in the manufacture of steel and iron wire exceeds or even equals that obtained by exposing layers of ferrous sulphide to air and rain and concentrating the lixivium and allowing it to crystallise.

Rich deposits of tin-stone are now worked in Tasmania. It may be asked whether the portion of this work treating of organic chemistry might have been rendered fuller and more instructive if less space had been devoted to graphic formulae. As it is the organic bases receive but a scanty notice. It is certainly true that vanillin is now made artificially from the inner bark of pine trees, but the natural product is still able to hold its own.

Caoutchouc is not peculiar to the sap of *Siphonia elastica*, but is found also in that of *Ficus elastica* (India) and *Hovea elastica* (Tropical Africa). Not improbably a fourth rubber-yielding tree will be found in New Guinea or the tropical regions of Australia.

Tannin is a substance, or rather a group of substances, very imperfectly known.

The cautions found *passim* in this book concerning explosives and poisons are very judicious. Prof. Hart may, perhaps, be considered to have written from a too exclusively American point of view; but among medium-sized text-books we should certainly give his work the preference to a vast number of others.

Everybody's Medical Guide. A Handbook of reliable Medical Information and Advice. By M.D. (Lond.). London: Saxon and Co. Pp. 122.

THIS little and handy book is, as we are candidly told in the preface, not designed to supersede the physician, whose advice is always to be preferred. Quack medicines and their accompanying pamphlets generally disappoint the purchaser because they fail in the capital point of diagnosis. It is here remarked that "one of the causes why Englishmen suffer so frequently from constipation is that they have such unbounded faith in advertised pills." It is amusing to read that Professor X Y's pills must be perfectly harmless as they are purely vegetable. The ignorance which can permit a compounder of medicines to pen such a sentence appears almost criminal if we

remember that no mineral is nearly as poisonous as the vegetables belladonna, foxglove, hemlock, nux vomica, &c. Among the possible causes of diarrhoea we find no mention of brown bread. To persons having a tendency to constipation such breads may be beneficial; but in others the particles of bran, however finely ground, produce an irritation which leads to chronic diarrhoea.

We find that not a few "proprietary articles" are here recommended, such as zymine, Kepler solution of cod-liver oil, hazeline, Wyeth beef-juice, &c. We are glad to find it here laid down that the use of "antipyrine" is not without danger.

This book may be safely recommended, especially to persons residing in remote country districts.

A Guide to Practical Chemistry for the Conjoint Board.
By PERCY A. E. RICHARDS, F.I.C., F.C.S. London: Baillière, Tindall, and Cox. 8vo., pp. 57.

FORTUNATELY this little book is provided with a rather more explicit title, or we might suppose that the author was guilty of satirising the Conjoint Board. The second title runs "Guide to the Examinations in Practical Chemistry for the Conjoint Board," thus showing that the modicum of chemical lore herein contained was destined for the examinees but not for the Board itself. In all sober sadness we must ask whether such a book can have any *locus standi*?

CORRESPONDENCE.

ARGON AND HELIUM.

To the Editor of the Chemical News.

SIR,—I observe on p. 180 of the present volume of the CHEMICAL NEWS a statement by Herr Siegfried Friedländer to the following effect.

"Crookes has hitherto pointed to the possibility of the compound nature of argon, in reliance upon spectroscopic investigation. J. M. Eder and E. Valenta consider this view as not excluded. But whilst the last mentioned investigators have examined only the red spectrum of argon, Crookes has observed both spectra, of which the red one is best visible at a pressure of 3 m.m., and at a reduced pressure changes into blue. Crookes has shown that it is not easy to obtain the blue spectrum quite free from the red, whilst in some circumstances the red spectrum does not change into the blue. Armstrong, indeed, thought that this need not be recognised as an evidence of the composite character of argon, since also nitrogen, hydrogen, and oxygen display such spectra. But as hitherto in these elements both spectra have never been seen simultaneously, Armstrong's view need not be accepted as a strict proof of the elementary nature of argon. I myself regard the phenomenon observed, that both the spectra of argon appear simultaneously, as one of the weightiest proofs that Lord Rayleigh and Prof. W. Ramsay have revealed two new elements by their discovery of argon."—*Zeitschrift für Physikalische Chemie*, xix., p. 657, and CHEMICAL NEWS, lxiv., p. 180, 1896.

The statement that both spectra of hydrogen, nitrogen, and oxygen have never been seen simultaneously is, I believe, contrary to fact. In the case of nitrogen it certainly is, because I have photographs in my possession taken in the year 1879 which show the two spectra of nitrogen obtained simultaneously from the one spark discharge in air, and not in a vacuum tube.

A reference to the *Proceedings of the Royal Society*, lviii., p. 293, Jan. 31, 1895—"The Spectrum of Argon as it appears in the Spark-Spectrum of Air,"—will show that

the concluding sentences of my paper are in the following words:—

"I do not attribute much importance to the fact that argon gives two spectra; the red appears to be the spectrum of the first order, or the spectrum of the lower temperature which corresponds thereto; the blue is the line spectrum, or spectrum at the higher temperature. I have photographed simultaneously from the same spark the two spectra of nitrogen as rendered by atmospheric air. It is therefore more likely that argon is one substance and not two. Whether it is a compound or an element is a question into which the following considerations may enter. There are at present no gaseous substances known which can withstand the temperature of the condensed spark without exhibiting the spectra of one or other of the elements of which it is composed. If, therefore, argon were N_3 it would disclose the spectrum of nitrogen. As the spectrum is not that of any known substance, it follows that, if a compound, it is a compound of a new element."

I have elsewhere shown how band spectra passed into line spectra (*Phil. Trans.*, clxxxv., pp. 161-212, 1894), and are related to each other, and it is easy to account for the two argon spectra being spectra of one substance.

I merely wish to point out that a serious error appears to have been made in a statement which has received a wide publication and which is not contained in the original literature on the subject.—I am, &c.,

W. N. HARTLEY.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxliii., No. 14, October 5, 1896.

Explosive Properties of Acetylene.—MM. Berthelot and Vieille.—The authors have considered it useful and necessary to define more completely, from a theoretical point of view, and by precise experiments, the explosive character of acetylene, and to signalise, from a practical point of view, what accidents may be produced in the conditions of its use. We must add that these inconveniences do not seem to counterbalance the advantages presented by this illuminant, or to limit its use. It is easy, in fact, to avoid these risks by suitable arrangements. Such as, on the one part, the operator avoids a too sudden escape of the compressed gas, and, on the other hand, takes care to absorb the heat produced by the compressions and internal reactions of the apparatus so as to prevent any notable rise of temperature.

Correction to a Paper on the Homogeneity of Argon and Helium.—Prof. W. Ramsay and J. N. Collie.—In a paper laid before the Academy on July 27th we committed an error which we must rectify. We had supposed that when a mixture of the two gases was submitted to diffusion we did not succeed in obtaining both in a state of purity, but that there always remained a mixture of the two gases in certain proportions, according to their densities. It is true that if we take a mixture of 1 part of hydrogen and 4 parts of oxygen the two gases pass through the permeable walls, so that equal quantities of both gases pass in the same time. This fact does not hinder their separation by means of diffusion. The densities calculated for the various fractions of helium are not those which we mentioned. On the contrary, the density of the heavier gas must be 2.133, and that of the lighter 1.874. The fact remains that we have succeeded separating helium into two parts.

On Beans.—M. Balland.—The bean, especially after decortication, is one of the most nitrogenous foods. The nitrogenous matter in the bean reaches 22.95 per cent.

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1927.

ON "TWIN-ELEMENTS."*

By RICHARD LORENZ.

I APPLY the name "twin-elements" to simple bodies whose atomic weights approach each other very closely in magnitude. The properties of such elements display manifold mutual relations. As the type of such twins we may regard cobalt and nickel. Their atomic weights are nearly equal, their chemical behaviour and occurrence show great similarity, and their separation presents difficulties. But whilst this couple has often been viewed as intimately connected, the fact has been overlooked that other elements bear, as we are about to show, a similar relation.

Of all the elements known to us a great number form such twin pairs in a very striking manner. In order to find such twin elements, let us suppose all the elements arranged according to the magnitude of their atomic weights. We consider the differences between such successive pairs. It appears that this difference is not greater than 1·4 units, in most cases smaller than 1.

The twin elements appear at once if we plot out the elements on a right line according to their atomic weights in such a manner that those with even atomic weights lie on one side of the line and those with odd atomic weights lie on the other side. For this purpose we must round off the atomic weights. In this manner we arrive at the accompanying table, referring the atomic weight of the elements to O = 16. The rounding off of the elements has been adopted only to facilitate a general view, and is by no means required to establish the regularities under consideration. In every case an odd and an even number form a twin group.

We find first boron and carbon. Taking O = 16, find the atomic weight of carbon = 12·003, and that of boron 11·0. The difference of both is 1·003. The two elements therefore are twins. It scarcely requires mentioning that here there exist manifold similarities. Both elements rank among the least fusible known. They both assume the amorphous, graphitoid, and diamond-like state, and in the latter they crystallise together, forming the boron diamond. Both of them do not conform to the law of Dulong and Petit. Sodium and magnesium form a twin pair. Mg = 24·38, Na = 23·058; difference = 1·322. These elements also display manifold similarities. The two following elements, aluminium and silicon, are twins. Their atomic weights are 28·40 and 27·08; difference 1·32. Sulphur and phosphorus also are twins. S = 32·063, P = 31·03; difference 1·033. In a chemical respect the two elements are readily comparable. Potassium and calcium are twins; their atomic weights are 40 and 39·136. Their joint occurrence and many of their relations are chemically manifest. Further twin pairs are chromium and vanadium, with atomic weights 52·15 and 51·21; difference 0·94. Also manganese and iron, with the atomic weights 55·09 and 56·0; the difference 0·91. There is no chemical objection to their juxtaposition. The twin pair cobalt and nickel have been already mentioned. Selenium and bromine have the atomic weights 79·67 and 79·963; difference 0·293. As regards this chemical behaviour they may be well compared with the twin pair S, P. This pair is again formed of two non-metals. The following pair is silver and palladium, with the atomic weights 107·938 and 106·7; difference 1·238. Antimony and tin are also twins; the atomic weight of

tin, according to the trustworthy determinations of Classen (O=16), is 119·1, and that of antimony 120·29; difference 1·19, being therefore twins. Both are "semi-metals," and are especially characterised by the behaviour of their sulphides, in consequence of which they follow each other analytically. Tellurium and iodine vary the successive order of their position, in consequence of different determinations of their atomic weights, as is the case with cobalt and nickel. If we take tellurium = 127·6 (Staudenmeier), or in round numbers 128, the difference of their atomic weights (as the atomic weight of I = 126·864) is 0·736 to 1·136; in any case these elements are twins. Chemically they have many similarities. Both are heavy non-metals, and behave to each other like bromine and selenium, or sulphur and phosphorus. The next twins are tungsten and tantalum; atomic weights 184·0 and 182·8; difference 1·2. Lead and bismuth are twin elements, with the atomic weights 206·91 and 206·911, and the difference 1·099.

Hence we have succeeded in finding fourteen pairs, therefore twenty-eight elements which may be regarded as twins:—

		Atomic weight.	Difference.
1.	{ Boron	11·0	
	{ Carbon	12·003	1·009
2.	{ Sodium	23·058	
	{ Magnesium	24·38	1·322
3.	{ Aluminium	27·08	
	{ Silicon	28·40	1·32
4.	{ Phosphorus	31·03	
	{ Sulphur	32·063	1·033
5.	{ Potassium	39·136	
	{ Calcium	40	0·864
6.	{ Vanadium	51·21	
	{ Chromium	52·15	0·94
7.	{ Manganese	55·09	
	{ Iron	56·0	0·91
8.	{ Nickel	58·71	
	{ Cobalt	59·37	0·66
9.	{ Selenium	79·07	
	{ Bromine	79·963	0·893
10.	{ Palladium	106·7	
	{ Silver	107·938	1·238
11.	{ Tin	119·1	
	{ Antimony	120·29	1·19
12.	{ Iodine	126·864	
	{ Tellurium	127·6	0·736
13.	{ Tantalum	182·8	
	{ Tungsten	184·0	1·2
14.	{ Lead	206·91	
	{ Bismuth	208·01	1·099

We may therefore enounce the proposition:—A great number of elements have atomic weights which approach each other very close in pairs, and differ from each other by at most 1·4 units; the proportions of these elements have manifold relations.

The Distribution of the Twin-Elements over the Series of Atomic Weights.

If we consider the position of the twin-elements over the series of numbers, we see that a great part of them follow each other in immediate succession. Thus, e.g., there follow upon [Na, Mg] [Al, Si], and [P, S]. There then succeed each other [V, Cr], [Mn, Fe], and [Ni, Co]. The twins just named are so distributed that both their even-numbered and their odd-numbered elements differ from each other by the round number 4. Thus we have—

	Difference.		Difference.
Na 23·058	4·022	Mg 24·38	4·02
Al 27·08		Si 28·40	
P 31·0	3·95	S 32·063	3·663

* Zeit. Anorganische Chemie.

Further—

	Difference.		Difference.
V 51.21	} 3.88	Ca 52.15	} 3.85
Mn 55.09		Fe 56.0	

If we now extrapolate the system of twins found here over the entire series of atomic weights,—i.e., if we assume that each pair of twins differs from the foregoing pair in round numbers by the atomic weight 4 or multiple of 4, we arrive at the surprising result that all the fourteen pairs of twins hitherto found fit into this scheme.

The atomic weights (in round numbers) of their elements differ always from each other by 4 or a multiple of 4.

The laterally adjacent elements of the above table are twin elements, (e.g., B, C, or Mn, Fe); those which stand beneath each other are arranged according to the magnitude of their atomic weight.

The Distribution in the Series of Numbers of those Elements which do not form Twins.

In the foregoing chapter we have seen that if we extrapolate over the entire series of numbers the scheme according to which some successive twins succeed each other, we arrive at all the other twin-elements, but there is a further consequence.

The single elements situate between the pairs of twins are found in the places required by the twin rule. This holds good for almost all the known elements, and it is particularly to be noted that it holds good most decidedly where the atomic weights are most certainly known, and does not hold good (with few exceptions) where the atomic weights are less accurately known.

Thus, e.g., phosphorus and sulphur are a twin pair [31, 32]. The following twin pair should have in round numbers the atomic weights [35, 36], and the next [39, 40]. The last is, in fact, formed by the elements potassium and calcium, but the intermediate space is unoccupied. But between sulphur and potassium lies chlorine, with the atomic weight 35.453, exactly in the middle of the twin pair [35, 36]. In like manner we find copper, arsenic, strontium, molybdenum, &c., in the places of twins.

(To be continued).

ON NEW SALTS OF COBALT AND NICKEL.
(A PRELIMINARY COMMUNICATION.)

By NAGENDRA CH. NÂG.

WHILST examining different specimens of bromine in March last, I remarked on a peculiar green colouration in the solution of a cobalt salt. In one experiment bromine with potassium carbonate was added to the solution of cobalt chloride in the expectation of the formation of a hypobromite. But there was formed a green solution like that of a nickel salt. This green solution of a cobalt salt was so striking a fact that I showed it to Professors Pedler and Rây, and they were not acquainted with any cobalt compound of this colour. They advised me, therefore, to undertake experiments for its isolation.

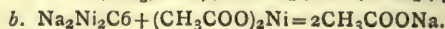
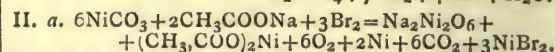
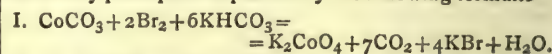
In order to obtain this compound free from potassium chloride, we precipitate cobalt carbonate with an excess of potassium bicarbonate and add bromine. There ensues a strong liberation of carbonic acid, whilst the cobalt carbonate slowly dissolves with a green colour. That this new compound is no bromine combination appears from the fact that it is precipitated along with the excess of bicarbonate on shaking the concentrated solution with alcohol and ether. The filtrate contains all the bromine as a bromide, and may be separated from the new compound by decantation. It is, however, very unstable after precipitation, even in an aqueous solution,

which is probably due to the presence of alcohol. Pressing between filter paper was also not of much use, and all attempts at isolating the new substance proved unsuccessful.

The compound seems to be an oxidation product, perhaps corresponding to the ferrates. If we allow the solution of the compound precipitated by alcohol and ether to stand for some time it is reduced, and displays dichroism, probably due to the presence of a violet-coloured precipitate. If we add to the green solution yellow ammonium sulphide or hydrogen sulphide, there is formed first a deep brown solution, which probably contains a lower oxidation product. It is then further reduced, and there appears a deposit. Ammonia alone likewise reduces it, and the green colour is changed with a probable production of cobalt ammonium compounds.

Experiments to obtain a corresponding nickel compound were unsuccessful. This fact is in accordance with the theory of Mendeleeff, according to which nickel is more electropositive than cobalt.

If instead of treating cobalt carbonate with potassium bicarbonate and bromine we add sodium acetate with bromine, there is formed a dark brown solution. The same experiment gives with salts of nickel a solution similar in colour to potassium bichromate. On boiling the solution of the nickel salt a part of the solution falls as a violet precipitate, and there remains a neutral liquid of an apple-green colour. In such circumstances the salts of cobalt give no precipitate. These, as above suggested, seem to be lower oxidation products, for if we add to the brown solution of a cobalt salt containing bromine in excess potassium bicarbonate, the green solution reappears. That in the case of nickel only the lower products of oxidation appear, and that even these are decomposed on boiling, is explained by the more basic character of nickel. The formation of the salts may perhaps be explained by the following formulæ—



—*Zeitschrift für Anorganische Chemie.*

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INCANDESCENT gas lighting, which consists in suspending fire-proof luminous substances within the flame of a Bunsen burner, has been carried out hitherto in several different ways.

The illuminating properties possessed by various metallic oxides, such as those of the zirconium, lanthanum, yttrium, thorium, and magnesium, have suggested the idea of making these oxides serviceable as luminous bodies.

The distinctive features of the various metallic oxides hitherto employed have been precisely determined from the points of view of both physical science and chemistry. These oxides are derived from corresponding ores, such as thorite, cerite, gadolinite, zircons, and the like.

The treatment of these ores is a question which has not as yet been fully cleared up, and I shall not attempt to deal with it, inasmuch as my own efforts have been directed to the study of other minerals.

But the numerous experiments which I have made have enabled me to discover and so satisfy myself of the

presence of a novel illuminating body (I will refer to it under the letter A) in a special ore of a sandy nature, obtainable at different places and known as monazited sand.

This body has properties different from those possessed by the substances used hitherto.

The ore, which possesses a sandy appearance, is really rich river loam found in small ruby-like pebbles.

The following is an example of an analysis made on a sample of this substance:—

(SiO ₂) Silica	69.7	per cent.
(P ₂ O ₅) Phosphoric acid	6	"
(Fe ₂ O ₃) Iron	1.92	"
(Al ₂ O ₃) Alumina	15	"
Cerium, lanthanum, didymium, about ..	2.13	"
Moisture	2.05	"
Lime, magnesia, and other miscellaneous matter, about	2	"
A body	1.80	"

This new body, A, enters into the composition of the ores named in the proportion of from 1.5 to 6 per cent, according to the sample dealt with.

Treatment.

The composition indicated above necessitates special methods of treatment, having for their object to eliminate any harmful substances which the body treated may contain.

The purity of this body is the main condition upon which a satisfactory yield depends.

The ore, on having been porphyrised, is slowly melted in suitable furnaces, with an addition of carbonate of sodium in the proportion of one part of ore for every two parts of carbonate. This operation, which takes about three hours to complete, is intended to convert the oxides into insoluble carbonates.

After cooling, the powdered mass is lixiviated; thus, by means of decantation, the elimination of the silicates and phosphates of sodium is proceeded with.

When the carbonates are exhausted by the water, they are subjected to the action of the sulphuric acid, the surplus of which is eliminated by slow calcination; the sulphates are dissolved in cold water and precipitated by means of ammonia. The precipitate, on being washed, is dissolved in hydrochloric acid, care being taken to properly neutralise it.

The greater part of the iron and alumina is then removed by precipitating it by means of oxalic acid.

The insoluble oxalates are converted into sulphates, when partial calcination in a muffle-furnace is proceeded with.

This calcination is interrupted at a certain period of the operation, which, however, can only be determined by taking into account the appearance of the material under treatment, the proper time for this being when the greater part of the acid has been eliminated. The sulphates obtained are then pulverised and put in cold water in small quantities, so that the saturation stage is, as nearly as possible, reached.

The solutions obtained is then precipitated by means of ammonia, whereby magnesia and the salts of lime are eliminated. Then, by filtering, a gelatinous precipitate of oxides is obtained, which is dissolved in sulphuric acid.

The sulphuric solution obtained, having had sulphate of sodium in solution, saturated while cold, added to it, is used as a precipitating medium, there being crystals in suspension in the mass, and the saturated solutions being allowed to digest for from five to six hours, thus the group, cerium, lanthanum, didymium, is precipitated.

The double sulphates thus obtained are filtered and then thoroughly washed.

In order to remove thorium, the solution is made in sulphuric acid, and the precipitate obtained by means of sulphate of potassium.

Thus all the bodies mentioned above, as being present with the A body, may be eliminated.

Now the principal operation of the process has to be commenced. It consists in precipitating the solution by means of hyposulphite of sodium in the condition of a concentrated solution. This operation is started with a slight action of heat. When the boiling point is reached, the A body is precipitated first. The body obtained contains as impurities small quantities of ytterite earths, principally ytterbia.

It only remains after this to effect a most thorough washing of the hyposulphite thus obtained, using cold water for the purpose. After the washing a solution is made in hydrochloric acid.

A reaction with sulphocyanide of ammonium will at that moment show whether there are any traces of iron left, and these, if present, may then be eliminated by the ordinary methods.

In the same way, traces of other metallic substances may be eliminated by means of a current of sulphuretted hydrogen sent into the solution of hydrochloric acid.

After precipitation by means of ammonia, the body is energetically washed with distilled cold water.

By such means a body is obtained which in itself is luminous, and which is made use of in the manner which I will now describe.

Generally speaking, the oxides employed for illuminating purposes, as well as the body to which I have referred just now, produce light which is illuminating and radiating only to a certain degree.

Radiation which constitutes the illuminating power proper, and more particularly the brilliancy desirable in a luminous body, is obtained owing to the molecular conditions which I have found to be realisable with exceptional ease in a body which, after many trials, I have discovered to be oxide of zinc. Any other body fulfilling the same conditions may, however, be employed without departing from the principle of the inventions.

Oxide of zinc, which upon being heated at an ordinary temperature assumes a greenish-yellow hue, when subjected to the heat of a Bunsen burner, becomes phosphorescent as it were. It is sufficient to add a small percentage of it to the illuminating solution.

I employ a nitric solution of the oxide in question.

After a fabric, which should be as fibrous as possible, has been impregnated with the said solution, when the wick thus formed has been incinerated, the decomposition of the nitrates will take place under the most favourable conditions conceivable.

Part of the oxide of zinc, the surplus thereof, is volatilised, while the remainder will be in that molecular condition referred to just now.

It is not impossible to use other oxides which, if employed under certain conditions, and mixed or combined in a certain definite manner, and either combined or not with the body A, may form novel bodies.

The fabric which I employ is made of special thread or filament, such as the fibres of flax, china grass, or the like, and it should have about 90 meshes per square centimetre. It is washed in a one-tenth solution of hydrochloric acid, and then with water having a slight amount of ammonia incorporated in it.

The fabric after drying is cut into strips of say 20 centimetres, and strengthened at their upper part with a strip of muslin or tulle.

Impregnation may be advantageously substituted by aspersion, by means of a special injector, which process offers the advantage of not necessitating protracted handling of the fabric whereby certain impurities might find their way into it.

The bath employed is a nitric aqueous solution, containing as much as 10 per cent of the luminous body. Each wick should absorb at least 6 cubic centimetres.

After the wick has been placed on a special form of mould, it is secured to a hanger of nickel by means of an asbestos thread.

A Bunsen flame is rapidly and circularly passed round the upper portion of the said wick, while another burner is worked from below. Incineration will then take place, and the earths will form gradually. By such means a skeleton is obtained, which is placed over a burner for about half-an-hour in order to secure complete calcination; the wick is then in readiness for being supplied in a marketable form, and may be fitted to any burner.

The novel illuminating body, which I have referred to as A, I have named "Lucium."

Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I declare that what I claim is—

1. For incandescent gas lighting a new body derived from monazite sands, substantially as hereinbefore described.

2. For incandescent gas lighting the body A referred to in the preceding claim, in combination with a small percentage of oxide of zinc or other body capable of imparting the necessary intensity and power of radiation as hereinbefore specified.

3. The purification of the A body, referred to in the first claim by treating monazite sands by oxalic acid, sulphate of sodium, sulphate of potassium, and hyposulphite of sodium, substantially as described.

4. For incandescent gas lighting the combination of the aforesaid body A (either alone or in combination with other bodies, as indicated in the second claim) with fibres or filaments substantially as and for the purpose hereinbefore specified.

SOURCES OF ERROR IN VOLHARD'S AND SIMILAR METHODS OF DETERMINING MANGANESE IN STEEL.*

By GEORGE AUCHY.†

VOLHARD'S method of determining manganese is generally considered a very accurate one; nevertheless, that the accuracy of the process is strictly dependent upon certain conditions and precautions not pointed out by the author, and not generally recognised (so far as the writer is aware) seems proved by the experience with the method and with Stone's modification of it, which follows:—

Stone's Modification.

Mr. Geo. C. Stone makes a very considerable saving in time by omitting the evaporation with sulphuric acid, and precipitating the iron immediately with zinc oxide as soon as solution of the drillings in nitric acid is effected.‡ But in Volhard's original article, as also in Blair's "Chemical Analysis of Iron," it is directed to destroy the carbonaceous matter by evaporation to dryness and strongly heating, or by evaporation with sulphuric acid till fumes of the latter come off, and as previous to the appearance of Mr. Stone's paper the writer—on testing this point by dissolving in sulphuric acid with enough nitric added to oxidise the iron and help to effect the solution of the drillings and omitting the evaporation—had obtained results several hundredths higher (although Volhard's objection to organic matter is that it hinders the balling together of the manganese dioxide in titration) than those obtained from the same samples by the regular process, it was judged that this precaution was not a useless one; and after reading Mr. Stone's article it was therefore con-

sidered well, as a precaution, to test his process also in this particular, and for that purpose the following determinations were made:—

TABLE I.

No.	Carbon. Per cent.	Volhard's method. Per cent.	Stone's modification. Per cent.
476	0.585	0.46	0.53
495	0.80	0.57	0.65
503	0.228	0.423	0.45
505	0.225	0.49	0.52
483	0.17	0.43	0.51
486	0.185	0.54	0.61
507	0.315	0.44	0.44

The results of Stone's method were very considerably higher than those by the regular method, except in the case of 507. But in the case of 507 it was noted that in making the precipitation of the iron by the zinc oxide a large excess had been accidentally used, while in all the other determinations the zinc oxide had been added in amount sufficient to precipitate the iron merely; and it was therefore thought advisable to see whether the considerable differences in the results by the two methods—Volhard's and Stone's—was not due to this fact (insufficient neutralisation in the latter) before attributing it to the organic matter undestroyed in Stone's method. The above determinations were therefore repeated, using in each case not only enough zinc oxide to coagulate the solution and precipitate the iron as directed, but also enough in excess of this amount to turn the brownish red colour of the iron precipitate to a light brown. The results follow:—

TABLE II.

No.	Carbon. Per cent.	Volhard. Per cent.	Stone. Zinc oxide in coagulation. Per cent.	Stone. Zinc oxide in large excess. Per cent.
503	0.228	0.423	0.45	0.45
505	0.225	0.49	0.52	0.51
483	0.17	0.43	0.51	0.45
486	0.185	0.43	0.51	0.45
486	0.185	0.55	0.61	0.58
486	0.185	0.54	0.61	0.58
476	0.585	0.46	0.53	0.47
495	0.80	0.57	0.65	0.60
471	0.105	0.38	—	0.40
480	0.10	0.35	—	0.36
493	0.57	0.46	—	0.47
507	0.315	0.435	—	0.44
153	0.50	0.64	—	0.70
153	0.50	0.64	—	0.67
153	0.50	0.64	—	0.69
155	0.40	0.56	—	0.56

These results show that when the zinc oxide is added merely to coagulation and precipitation of the iron, leaving the solution probably faintly acid, the manganese is afterward precipitated, not according to the theoretical formula, but with result too high; and that to insure the correct precipitation of the manganese it is necessary to add the zinc oxide in large excess, so that the solution is thoroughly neutralised when titrated.

It will, however, be noted that with this precaution, observed results in this table are nevertheless a few hundredths per cent higher than by Volhard's method.* Is this difference due to the undestroyed carbonaceous matter? It was thought probable, but, to make sure, some of the tests were repeated with oxidation of the

* *Journal of the American Chemical Society*, xviii., No. 6, p. 498

† In the *Journ. Am. Chem. Soc.*, xviii., 406, I omitted to state a precaution used in the manner of performing Drown's sulphur method there described. The solution from the Troilus' bulb is heated to boiling (preferably with the previous addition of permanganate solution) before filtering into it the hydrochloric acid solution from the graphic residue. This is to oxidise any sulphur that may be present as sodium sulphide.

‡ *Journ. Amer. Chem. Soc.*, xviii., 228. Mr. Stone finds that hydrochloric acid solution also works well.

* It was later seen that the accuracy of the regular Volhard process was also dependent upon certain conditions; and the results by this method, given in these two tables, are the corrected results obtained later by checking with the colour method according to Table VI. So that in Tables I. and II. the comparison is really with the colour method rather than with Volhard's method. As explained under Table VI., there was not enough left of the samples for gravimetric tests. For a comparison of Stone's method with the gravimetric see Table XI.

carbonaceous matter by addition of lead dioxide to the boiling nitric acid solution of the drillings (the excess destroyed by ferrous sulphate and the excess of the latter oxidised by continued boiling of the nitric acid solution).^{*} These results should be lower if carbonaceous matter has any influence. They were not lower, as the following table shows, and hence it is indicated that carbonaceous matter does not interfere. It is true that in one case (483) the result obtained by oxidation of the carbonaceous matter is lower, but the reason for this will appear later on.

TABLE III.

No.	Carbon. Per cent.	Stone. With carbon not oxidised.	Stone. With carbon oxidised.
		Per cent.	Per cent.
480	0.10	0.36	0.37
507	0.315	0.44	0.44
155	0.40	0.56	0.55
155	0.40	0.56	0.57
155	0.40	0.56	0.56
155	0.40	0.56	0.56
153	0.50	0.70	0.68
483	0.17	0.45	0.41

Since the slightly high results obtained by Stone's method, in Table II., are not due to the undestroyed carbonaceous matter, they must be due to the fact of titration in nitric acid solution. The following determinations of manganese in solutions containing no organic matter, and in which the amount of manganese was known (made by taking definite amounts of standard permanganate solution) are confirmatory of this conclusion:—

TABLE IV.

No.	Manganese taken.	Manganese found.
	Per cent.	Per cent.
1.	0.40	0.41
2.	0.40	0.41
3.	0.40	0.41
4.	0.40	0.41
5.	0.40	0.41
6.	0.40	0.41
7.	0.40	0.42
8.	0.40	0.42
9.	0.80	0.81
10.	0.80	0.82
11.	1.20	1.24
12.	1.20	1.22
13.	0.80	0.81
14.	1.20	1.22

Here, then, is a second precaution to be observed in Stone's method: a correction of the result by one or two hundredths per cent must in each case be made. But still other precautions are necessary, as will appear.

(To be continued).

ON THE INVERSION OF SUGAR BY SALTS.[†] No. II.

By J. H. LONG.
(Continued from p. 204).

Potassium Alum.

SOLUTIONS of this salt invert very rapidly. A sample of pure alum was crystallised several times from distilled water to secure a product free from traces of uncombined sulphuric acid, sometimes present in the commercial article. This carefully purified salt was used in all the inversion tests. In the tables below, *t* refers to the time in minutes, and

^{*} The lead dioxide and the ferrous sulphate used were tested for manganese.

[†] From the *Journal of the American Chemical Society*, xviii., No. 8, August, 1896.

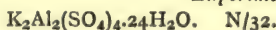
Experiment 1.



In 250 c.c., 50 grms. of sugar + 0.617 grm. of alum.
 $A = 33.03^\circ$.

<i>t</i> .	<i>a</i> .	<i>x</i> .	Log. $\frac{A}{A-x}$.	$\frac{1}{t}$ log. $\frac{A}{A-x}$.
0	24.73°	—	—	—
15	20.15	4.58°	0.06483	0.00432
30	16.16	8.57	0.13045	0.00434
60	9.75	14.98	0.26243	0.00437
90	4.85	19.88	0.39998	0.00444
120	1.25	23.48	0.53891	0.00449
150	-1.30	26.03	0.67581	0.00449
210	-4.88	29.61	0.98488	0.00468
270	-6.40	31.13	1.24016	0.00459
				0.00446

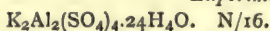
Experiment 2.



In 250 c.c., 50 grms of sugar + 1.234 grms. of alum.
 $A = 32.37^\circ$.

<i>t</i> .	<i>a</i> .	<i>x</i> .	Log. $\frac{A}{A-x}$.	$\frac{1}{t}$ log. $\frac{A}{A-x}$.
0	24.07°	—	—	—
15	17.83	6.24°	0.09300	0.00620
30	12.92	11.15	0.18339	0.00611
60	5.50	18.57	0.37026	0.00612
90	0.75	23.32	0.55349	0.00615
120	-2.48	26.55	0.74522	0.00621
150	-4.76	28.83	0.96114	0.00641
210	-7.00	31.07	1.39620	0.00661
270	-7.80	31.87	1.81117	0.00670
				0.00632

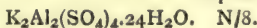
Experiment 3.



In 250 c.c., 50 grms. of sugar + 2.468 grms. of alum.
 $A = 31.25^\circ$.

<i>t</i> .	<i>a</i> .	<i>x</i> .	Log. $\frac{A}{A-x}$.	$\frac{1}{t}$ log. $\frac{A}{A-x}$.
0	22.95°	—	—	—
15	14.80	8.15°	0.13124	0.00875
30	8.79	14.16	0.26211	0.00873
60	1.07	21.88	0.52311	0.00872
90	-3.03	25.98	0.77304	0.00859
120	-5.64	28.59	1.06997	0.00891
180	-7.53	30.48	1.55533	0.00864
240	-8.15	31.10	2.31866	0.00966
				0.00886

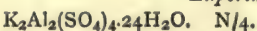
Experiment 4.



In 250 c.c., 50 grms. of sugar + 4.936 grms. of alum.
 $A = 30.03^\circ$.

<i>t</i> .	<i>a</i> .	<i>x</i> .	Log. $\frac{A}{A-x}$.	$\frac{1}{t}$ log. $\frac{A}{A-x}$.
0	21.73°	—	—	—
15	11.23	10.50°	0.18686	0.01245
30	4.45	17.28	0.37205	0.01240
60	-2.87	24.60	0.74276	0.01238
90	-5.95	27.68	1.10649	0.01230
120	-7.34	29.07	1.49529	0.01244
180	-8.18	29.91	2.39838	0.01332
				0.01255

Experiment 5.



In 250 c.c., 50 grms. of sugar + 9.872 grms. of alum.
 $A = 29.19^\circ$.

<i>t</i> .	<i>a</i> .	<i>x</i> .	Log. $\frac{A}{A-x}$.	$\frac{1}{t}$ log. $\frac{A}{A-x}$.
0	20.89°	—	—	—
10	10.89	10.00°	0.18216	0.01822
25	2.10	18.79	0.44820	0.01793
50	-4.70	25.59	0.90893	0.01818
90	-7.73	28.62	1.70936	0.01899
150	-8.25	29.14	2.76626	0.01844
				0.01835

under α is given the observed angle of rotation in degrees and hundredths.

An attempt was made to invert with a half normal solution, but at the temperature employed the rate was found to be too rapid for accurate observation.

With the first four solutions no difficulty was found in making accurate polarimetric observations in the 200 m.m. tube. The last solution, however, became finally somewhat coloured, and slightly turbid from precipitation of what appeared to be aluminum hydroxide. A portion heated 180 minutes became too turbid for direct reading, and had to be examined in the 100 m.m. tube after filtration. The rotation was found now to be -3.60° , corresponding to -7.20° for the 200 m.m. tube, instead of -8.25° or -8.30° . From the slight concentration due to the filtration a still greater negative value instead of a lower one should be expected. We have here an illustration of the fact referred to above, viz., that prolonged heating makes the end-point determination somewhat uncertain at times.

It is interesting to note the relation existing between the concentrations of the solutions and their rates of inversion in the above examples. For comparison, we call the lowest concentration unity and arrange them as follows:—

Conc.		K.
N/64	1	0.00446
N/32	2	0.00632
N/16	4	0.00886
N/8	8	0.01255
N/4	16	0.01835

Inspection of the table shows that the coefficient, K, increases rapidly with the concentration, but is not directly proportional to it. It is apparent that the numbers in the third column vary approximately as the square roots of those in the second, which is clearly shown in the next table:—

Conc.	K.	$K_1 \times \sqrt{\text{Conc.}}$
1	0.00446	0.00446
2	0.00632	0.00631
4	0.00886	0.00892
8	0.01255	0.01261
16	0.01835	0.01784

The regular results obtained from the aluminum salt are probably due in a measure to the inertness of the hydroxide toward sugar, as well as to the behaviour of sulphuric acid in inversion. The bases of the other salts examined below form combinations with sugar more or less readily, not only with saccharose, but also with the products of inversion, so that the normal results of the reaction may be modified in a manner difficult to compute. The rather rapid rate of inversion in the above points to a relatively great degree of hydrolysis in the alum. Walker and Aston (*loc. cit.*) found something similar in a half normal solution of the nitrate, studied at a temperature of 80° . From their polarisations a value of 0.0077 for K was found, and this was much in excess of the values found for other salts at the same time.

Ferrous Sulphate.

A sample of the purest obtainable sulphate was re-crystallised from water containing a trace of sulphuric acid, then dissolved in distilled water and precipitated by alcohol. The crystal meal secured was washed several times with alcohol and dried by fanning. The finished product was bright green and gave a nearly clear solution with pure water. It still held a trace of alcohol, as disclosed by the odour. The experimental solutions were made by dissolving the sugar first and adding to this syrup the weighed sulphate meal. The mixtures were shaken to complete solution without application of heat, and then poured into the tubes for inversion. The solutions soon became turbid on warming, and a minute amount of flocculent precipitate separated, making direct polarisation

impossible. The readings could be made therefore only after filtration, which was not without slight effect on the result. The total amount of separated hydroxide or basic salt was, and remained through the test, minute.

Experiment 6.

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. N/2.

In 250 c.c., 50 grms. of sugar + 17.38 grms. of sulphate.

$A = 17.12$.

t.	α .	α' .	Log. $\frac{A}{A-\alpha}$.	$\frac{1}{t} \log. \frac{A}{A-\alpha}$.
0	12.97	—	—	—
15	12.48	0.49	0.01261	0.00084
45	11.50	1.47	0.03899	0.00086
75	10.40	2.57	0.07064	0.00094
135	8.43	4.54	0.13382	0.00099
195	6.72	6.25	0.19727	0.00101
255	5.21	7.76	0.26222	0.00102
375	2.87	10.10	0.38716	0.00103
495	1.03	11.94	0.51917	0.00105
				0.00099

Experiment 7.

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. N.

In 250 c.c., 50 grms. of sugar + 34.75 grms. of sulphate.

$A = 17.10$.

t.	α .	α' .	Log. $\frac{A}{A-\alpha}$.	$\frac{1}{t} \log. \frac{A}{A-\alpha}$.
0	12.95	—	—	—
15	12.45	0.50	0.01289	0.00086
45	11.26	1.69	0.04520	0.00100
75	10.08	2.87	0.07980	0.00106
135	8.07	4.88	0.14593	0.00108
195	6.30	6.65	0.21388	0.00110
255	4.70	8.25	0.28606	0.00112
375	2.25	10.70	0.42682	0.00114
495	0.15	12.80	0.59953	0.00121
				0.00107

Other tests were made with a second preparation of ferrous sulphate from which the alcohol had not been as completely removed. For a half normal solution the coefficient 0.0094 was found, and for a normal solution the value 0.00100; both results being but a trifle lower than those obtained from the pure products. It is possible that the differences may be due to the presence of the trace of alcohol. In any case it is evident that with solutions as strong as those used the larger amount of sulphate inverts but little more rapidly than the smaller.

(To be continued).

THE APPROACHING JUBILEE OF SCIENCE TEACHING IN THE CITY OF LONDON SCHOOL.

ON Thursday, October 22nd, a preliminary meeting of Old Scholars was held in the library of the City of London School, for the purpose of considering the desirability of taking steps to celebrate the forthcoming Jubilee of Science Teaching at their school. There was a good attendance, and Dr. William Garnett was invited to take the chair. An original prospectus of Mr. Thomas Hall's first course of lectures, bearing date March 12th, 1847, was produced, which announced the determination of the then school committee to introduce the subject of Chemistry, with accompanying syllabus. Two of Mr. Hall's earliest pupils who were present—Messrs. J. C. Harker and J. Spiller—affirmed that they actually attended these lectures in 1847, and it was commonly believed that they constituted the first successful endeavour to introduce the study of natural science into the curriculum of a public school. Having regard to the large number of students who had been thus induced to qualify for entering the scientific professions, and the early date of such technical teaching,

it was thought that the Corporation of the City of London might possibly be inclined to join in the celebration of an event at once so interesting and creditable to the Municipal authorities.

Resolutions were passed, and an influential committee was formed to take steps in the direction indicated. Dr. W. H. Perkin, F.R.S., being elected chairman, Mr. Alexander Mortimer, M.A., treasurer, and Messrs. Henry Durham, F.C.S., and John Spiller, F.C.S., were requested to act as joint-secretaries. It was suggested that a "Hall Memorial Fund" should be raised for the purpose of instituting prizes, or founding a scholarship, for the encouragement of scientific studies. Also that, if possible, a *conversazione* should be held at some convenient date shortly before Easter, 1897.

THE SCIENTIFIC DEPARTMENT OF THE IMPERIAL INSTITUTE.

THE extended organisation of the experimental branch of the Scientific and Technical Research Department of the Imperial Institute is now nearly complete, and the whole of the west corridor of the second floor is occupied by well-equipped laboratories, instrument rooms, and sample examination rooms, whilst the recently appointed staff of skilled chemists is already engaged in the scientific and technical investigation of numerous Indian and Colonial products, which are likely to prove of commercial importance or of scientific interest.

The Winter Course of Lectures will be opened on Monday, November 9th, at 8.30 p.m., with a discourse by Professor Wyndham Dunstan, F.R.S., the recently-appointed Director of the Scientific Department, the subject of which will be "Illustrations of some of the Work of the Scientific and Technical Research Department of the Imperial Institute." After the lecture the Research Laboratories of the Department will be open for the inspection of visitors, and a number of interesting exhibits will be on view.

On November 16th Mr. William Crookes, F.R.S., will deliver the first of two illustrated lectures on the "Diamond Mines of Kimberley," in connection with which a number of specimens and experiments of great interest will be shown. Among other topics Mr. Crookes will discuss the nature and probable origin of the diamond, and will give an account of recent researches of his own. On the occasion of the first lecture Lord Loch will preside.

On the two remaining Monday evenings in November illustrated lectures will be given by Prof. J. W. Judd, C.B., F.R.S., the Dean of the Royal College of Science, on "Rubies, Natural and Artificial, with special reference to their Occurrence in the British Empire" (November 23rd), and by Dr. J. H. Bryan, F.R.S., on "Flight, Natural and Artificial" (November 30th).

Succeeding lectures, the dates of which will be duly announced, will be given by Prof. A. H. Church, F.R.S., Professor of Chemistry to the Royal Academy, on "Some Food-grains of India"; by Dr. Schlich, C.I.E., of the Royal Indian Engineering College, Cooper's Hill, on "The Timber Supply of the British Empire"; by the Hon. W. Pember Reeves, Agent-General for New Zealand, on "The Hot Springs District of New Zealand"; by Colonel Watson, R.E., on "Schools of Modern Oriental Study"; by Mr. A. Montefiore Brice, F.R.G.S., on "The Results of the Jackson-Harmsworth Expedition"; A course of three lectures by Dr. J. L. W. Thudichum, F.R.C.P., on "The Nature and Manufacture of Wine, with special reference to Colonial Wines"; by Prof. J. Norman Lockyer, C.B., F.R.S., on "How the British Empire aids in Solar Enquiries"; by Prof. W. E. Ayrton, F.R.S., on "Sixty Years of Submarine Telegraphy"; and by Mr. Spencer Pickering, F.R.S., on "The Woburn Experi-

mental Fruit Farm." These lectures are open to Fellows of the Institute, and to persons introduced by them.

INVESTIGATION TO DETERMINE WHETHER DIPHENYLIODONIUM AND THALLIUM NITRATES ARE ISOMORPHOUS.

By A. A. NOYES, Ph.D., and C. W. HAPGOOD, S.B.

THE great similarity in properties observed by V. Meyer (*Berichte der Deutschen Chemischen Gesells.*, xxvii., 502, 1592) between the salts of thallium and diphenyliodonium, $(C_6H_5)_2I.OH$, made it seem not improbable that they might be also isomorphous with each other. The matter seemed worthy of investigation, as only a few such cases of isomorphous replacement of single atoms by complex organic radicals are known.

According to the extended investigations of Retgers, by far the most reliable criterion of isomorphism is furnished by the power of the substances in question of forming homogeneous mixed crystals with the proportions varying continuously within wide limits. Consequently, the experimental method based on this principle as described by Retgers (*Zeitsch. fur Physikalische Chemie*, iv., 593) was followed, chemical analysis and specific gravity determinations being employed to determine the character of the crystals separating from the solution. Preliminary experiments showed that the largest and most perfect crystals were obtained with the nitrates when crystallised from alkaline solution. Saturated solutions of thallous nitrate in water and of diphenyliodonium nitrate (made as described by Hartmann and V. Meyer, *Berichte der Deutschen Chemischen Gesellschaft*, xxvii., 506) in a moderately strong aqueous solution of the free base, diphenyliodonium hydrate, were therefore prepared, mixed with each other in crystallising dishes in varying proportions, and allowed to stand in a vacuum desiccator till a sufficient quantity of crystals had separated. The solutions were mixed in the following proportions, the number of parts of the diphenyliodonium nitrate solution being given first:—10 : 1·1 ; 10 : 2 ; 10 : 5 ; 10 : 6·7 ; 10 : 10 ; 10 : 15 ; 10 : 20 ; 10 : 50 ; and 10 : 90.

The first crop from the last solutions consisted of two distinct kinds of crystals, one kind much lighter and the other much heavier than methylene iodide. In all the other cases only one kind of crystals, which were lighter than methylene iodide, was obtained. The specific gravity of these lighter crystals separating from each of the nine solutions was determined by the suspension method of Retgers (*Zeits. f. Phys. Chem.*, iii., 289), the value taken being that corresponding to the heaviest crystals of each lot. The results varied irregularly between 1·866 and 1·889. For the pure diphenyliodonium nitrate we found 1·868. For thallous nitrate Lamy (*Ann. de Chem. et de Phys.* (3), lxvii., 409) found 5·8. The lighter crystals were therefore in all nine cases practically pure diphenyliodonium nitrate. The heavier crystals from the last solutions were mixed together, dried at 100°, and analysed by heating in a crucible with concentrated sulphuric acid and igniting. Two separate determinations showed them to contain 99·83 and 99·93 per cent of thallous nitrate.

Thus the two salts crystallise out separately from the solution in the pure state, not in the form of mixed crystals. They are therefore not isomorphous.—*Technology Quarterly and Proceedings of the Society of Arts*, ix., p. 236.

Sir Charles Cameron.—On Friday last, 23rd inst., the Royal University of Ireland conferred the degree of M.D., *Honoris Causa*, on Sir Charles A. Cameron, ex-President, and Professor of Chemistry and Hygiene, R.C.S.I.

THE
ACTION OF LIGHT UPON DYED COLOURS.*

(Concluded from p. 207).

CLASS II.—FUGITIVE COLOURS. (Wool, continued).
Azo Colours.

Wool Book X.

Direct Cotton Colours.—

9. Benzo Cyanine 3B. Constitution not published.
11. Indoin Blue 2B. From Safranine and β -naphthol.
12. Metazurin B. Constitution not published.
14. Benzo Blue 3B. Constitution not published.
15. Benzo Red Blue G. Constitution not published.
16. Columbia Blue G. Constitution not published.
17. Chicago Blue R. Constitution not published.
18. Naphthazurin. Constitution not published.
23. Diamine Blue 2B. From benzidine and amido-naphthol-disulphonic acid H.
24. Diamine Blue 3B. From tolidine and amido-naphthol disulphonic acid H.
25. Benzo Cyanine R. Constitution not published.
26. Indazurin. Constitution not published.
27. Direct Blue B. From dianisidine, dioxy-naphthoic sulphonic acid, and α -naphthol- β -sulphonic acid.
28. Heligoland Blue 3B. Constitution not published.
29. Benzo Azurine G. From dianisidine, and α -naphthol mono-sulphonic acid NW. S. and J. 210.
30. Benzo Red Blue R. Constitution not published.
31. Columbia Blue R. Constitution not published.
32. Benzo Azurine 3G. From dianisidine, and α -naphthol-mono-sulphonic acid L. S. and J. 213.
33. Brilliant Metazurin OOO. Constitution not published.
34. Diamine Blue BX. From tolidine, α -naphthol-mono-sulphonic acid NW, and amido-naphthol-disulphonic acid H.
35. Diamine Blue B. From ethoxy-benzidine, β -naphthol- β -disulphonic acid, and α -naphthol-mono-sulphonic acid NW. S. and J. 205.
36. Heligoland Blue R. Constitution not published.
37. Oxamine Blue 3R. From tolidine, β -amido- α -naphthol- β -sulphonic acid, and α -naphthol- α -sulphonic acid.
38. Diamine Blue 3R. From ethoxy-benzidine, and α -naphthol-mono-sulphonic acid NW. S. and J. 206.
39. Azo Blue. From tolidine, and α -naphthol-mono-sulphonic acid NW. S. and J. 187.
43. Azo Navy Blue. Constitution not published.
45. Direct Blue Black B. Constitution not published.

Acid Colours.—

23. Azo Acid Blue B. Constitution not published.

Natural Colouring Matters.

Mordant Colours.—

Logwood (Al). Wood of *Hæmatoxylon campechianum*.

NOTES.—Azo acid blue acquires, on fading, a very red shade; turquoise blue 2B and glacier blue change to a green during the first period. Basile blue B and benzo blue 3B lose their bloom of colour during the first "fading period," the remaining dark greyish colour being moderately fast. Direct cotton colours, 12, 17, 18, 23, 24, 25, change from blue to grey during the first "fading period," and Nos. 15, 16, and 26 to 39 all acquire a marked reddish tint. On this account these colours might almost equally well be placed among the "very fugitive colours."

CLASS III.—MODERATELY FAST COLOURS. (Wool).

The colours of this class show distinct fading at the end of the second period (August 12 to September 3, 1895).

* Report of Committee, consisting of Professor T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Liverpool Meeting, 1896.

which becomes more pronounced at the end of the third period (September 3 to September 20, 1895). A pale tint remains at the end of the fourth period (September 20, 1895, to April 7, 1896), and at the end of a year's exposure the colour has entirely faded, or, at most, mere traces of colour remain.

Triphenylmethane Colours.

Wool Book X.

Mordant Colours.—

1. Chrome Blue (Cr). Oxy-carboxy-tetra-methyl-diamido-diphenyl-naphthyl-carbinol.

Wool Book IX.

Acid Colours.—

3. Patent Blue A. Calcium salt of *m*-oxy- (or *m*-amido)-tetra-alkyl-diamido-triphenyl-carbinol-sulphonic acid.
4. Patent Blue superfine. Ditto.
12. Alkali Blue. Sodium salt of mono- and di-phenyl-rosaniline-mono-sulphonic acid.
13. Alkali Blue 6B. Sodium salt of tri-phenyl rosaniline-mono-sulphonic acid.
14. Hoechst New Blue. Calcium salts of tri-methyl-triphenyl- β -rosaniline, di- and tri-sulphonic acids.
15. Methyl Blue MBI. Sodium salt of tri-phenyl- β -rosaniline-tri-sulphonic acid.
16. Water Blue 6B extra. Sodium salt of tri-phenyl-rosaniline-tri-sulphonic acid.
17. Bavarian Blue DBF. Sodium salt of diphenylamine blue-tri-sulphonic acid. S. and J. 300.
18. Bavarian Blue DSF. Sodium salt of diphenylamine blue-di- and tri-sulphonic acid. S. and J. 299.
19. Alkali Blue D. Sodium salt of diphenylamine blue-mono-sulphonic acid. S. and J. 298.
20. Alkali Blue R. Sodium salt of mono-phenyl-rosaniline-mono-sulphonic acid.
22. Soluble Blue pure. Sodium salt of tri-phenyl-rosaniline-tri-sulphonic acid.

Oxazine Colours.

Wool Book X.

Mordant Colour.—

5. Galloxyaniline DH (Cr). Chloride of dimethyl-phenyl-ammonium-dioxy-phenoxazine-carboxylic acid. S. and J. 340.

Wool Book IX.

Acid Colour.—

35. Gallanilic Blue R. Constitution not published.

Induline Colours.

Wool Book IX.

Acid Colours.—

26. Milling Blue. Sodium salt of anilido-iso-naphthyl-rosinduline-mono-sulphonic acid.
28. Naphthyl Blue. Sodium salt of anilido-phenyl-naphthinduline-sulphonic acid.
29. Naphthazine Blue. Sodium salt of tetra-methyl-diamido-dinaphthyl-diphenazonium-di-sulphonic acid.
30. Induline NN. Sodium salt of sulphonic acid of a Spirit Induline. S. and J. 366.
31. Indigen F liquid. Sodium salt of sulphonic acid of a Spirit Induline. S. and J. 365.
32. Induline 3B. Sodium salt of sulphonic acid of a Spirit Induline. S. and J. 366.
37. Fast Blue B. Sodium salt of sulphonic acid of a Spirit Induline. S. and J. 365.

Basic Colours.—

22. Toluyene Blue B. Constitution not published.
23. Indamine Blue N. Hydrochloride of β -amido-phenyl-amido-derivatives of a Spirit Induline.
31. Paraphenylene Blue R. Hydrochloride of amido-phenyl-induline.
32. Indophenine extra. Constitution not published.
33. Indophenine B. Constitution not published.

Azo Colours.

Wool Book IX.

Acid Colours.—

38. Blue Black B. From β -naphthylamine-mono-sulphonic-acid azo- α -naphthylamine and β -naphthol-disulphonic acid R. S. and J. 134.
39. Indigo Blue powder. From toluene-azo-naphthylamine and β -naphthol-sodium-disulphonate.

Wool Book X.

Direct Cotton Colours.—

5. Brilliant Sulphon Azurine R. Constitution not published.
6. Sulphon Cyanine. Constitution not published.
7. Sulphon Azurine. From benzidine-sulphon-disulphonic-acid, and phenyl- β -naphthylamine. S. and J. 182.
10. Sulphon Cyanine 3R. Constitution not published.
13. Brilliant Azurine 5G. From dianisidine and dioxynaphthalene- α -mono-sulphonic acid. S. and J. 215.
19. Naphthyl Blue 2B. From *o*-amido-diphenylic acid, and benzoyl-amido-naphthol.
20. Benzo-Indigo Blue. From dianisidine, α -naphthylamine, and dioxynaphthalene- α -mono-sulphonic acid (1:8).
21. Diamine Blue Black E. From ethoxy-benzidine, β -naphthol- δ -disulphonic acid, and γ -amido-naphthol-sulphonic acid.
22. Blue JCR. Constitution not published.
40. Benzo Black Blue R. From tolidine-disazo- α -naphthylamine and α -naphthol-mono-sulphonic acid NW. S. and J. 226.
41. Congo Fast Blue B. Constitution not published.
42. Benzo Black Blue G. From benzidine-disulphonic acid-disazo-naphthylamine, and α -naphthol-mono-sulphonic acid NW. S. and J. 225.
44. Congo Fast Blue R. Constitution not published.

Natural Colouring Matters.

Wool Book X.

Mordant Colour.—Logwood (Cr). Wood of *Hæmatoxylon campechianum*.

NOTES.—The Patent Blues become darker during the first two fading periods. Brilliant Sulphonazurine R acquires a decided reddish tint during the later stages of fading. The Sulphocyanines and Galloxyanines DH appear to be faster than the rest of the colours placed in this class, and do not change in hue during the fading process. The fastness of the Alkali Blues is probably greater than is usually supposed to be the case. The blue given by logwood with chromium is much faster than that obtained with aluminium mordant.

CLASS IV.—FAST COLOURS. (WOOL).

The colours of this class show comparatively little fading during the first, second, and third periods. At the end of the fourth period a pale shade remains, which at the end of the year's exposure still leaves a pale tint.

Triphenylmethane Colours.

Wool Book X.

Mordant Colour.—

9. Gallein (Cr). Oxidation product of pyrogallol-phthalein. S. and J. 335.

Wool Book IX.

Basic Colour.—

25. Gentiana Blue 6B. Hydrochloride of tri-phenyl-rozaniline.

Oxazine Colours.

Wool Book X.

Mordant Colour.—

7. Gallamine Blue (Cr). Product of action of nitroso dimethyl-aniline-hydrochloride on gallaminic acid. S. and J. 346.

Azo Colours.

Wool Book IX.

Acid Colour.—

36. Naphthol Blue Black. From *p*-nitraniline, aniline, and amido-naphthol-disulphonic acid H (1:8).

Induline Colours.

Acid Colour.—

33. Fast Blue 6B for wool. A sulphonated induline.

NOTE.—That Gentiana Blue 6B has proved to be fast is very remarkable, since the basic colours, and particularly those of the triphenylmethane group, are usually so fugitive. During the first fading period the bloom of the colour disappears, but the remaining colour fades very little even throughout the period of a whole year.

CLASS V.—VERY FAST COLOURS. (WOOL).

The colours of this class show a very gradual fading during the different periods, and even after a year's exposure a moderately good colour remains.

Oxazine Colours.

Wool Book X.

Mordant Colour.—

6. Cœlestine Blue B (Cr). Constitution not published.

Thiazine Colours.

Mordant Colours.—

10. Brilliant Alizarin Blue R (Cr). Constitution not published. A derivative of oxy-naphtho-quinone-imide.
12. Brilliant Alizarin Blue G (Cr). Constitution not published.

Oxyketone Colours.

Mordant Colours.—

2. Alizarin Blue WX (Cr). Di-oxy-anthraquinone-quinoline. S. and J. 255.
3. Alizarin Blue S powder (Cr). Sodium bisulphite compound of Alizarin Blue. S. and J. 256.
4. Anthracene Blue WR (Cr). Hexa-oxy-anthraquinone.
8. Alizarin Cyanine R (Cr). Penta-oxy-anthraquinone. S. and J. 249.
11. Alizarin Cyanine G (Cr). Action of ammonia on intermediate product in making Alizarin Cyanine R. S. and J. 250.
13. Anthracene Blue WG (Cr). Constitution not published.
15. Alizarin Indigo Blue SW (Cr). Sodium bisulphite compound of tetra- and penta-oxy-anthraquinolin-quinone-sulphonic acid. S. and J. 257.
16. Alizarin Cyanine Black G (Cr). Constitution not published.

Natural Colouring Matters.

Wool Book X.

Direct Colour.—

1. Vat Indigo Blue.

Additional Colouring Matters.

Acid Colour.—

2. Prussian Blue.

NOTES.—The great fastness of the Brilliant Alizarin Blues is remarkable, since they belong to a group of colouring matters which has not hitherto furnished fast colours. The same remark applies to Cœlestine Blue, although this colour is not so fast as the foregoing. The fastness of the various Alizarin Blues (oxyketone colours) is proverbial, and along with the colours just named they may well be regarded as worthy competitors of indigo for the production of fast blues. The chief difference of behaviour of Indigo Blue and some of the Alizarin Blues is that the latter tend to acquire a reddish tint, whereas the former does not.

The remarkable fastness of Prussian Blue on wool is such that the medium blue colour experimented upon has not perceptibly faded during a whole year's exposure,

and it may be justly considered as the fastest blue on wool with which we are at present acquainted; unfortunately it is sensitive to the action of alkalis.

GREEN COLOURING MATTER.

CLASS I.—VERY FUGITIVE COLOURS. (WOOL).

Wool Book XI.

Basic Colours.—

1. Capri Green G. Constitution not published.
11. Solid Green 3B. Zinc double chloride of dichlor-tetra-methyl-diamido-triphenyl-carbinol. S. and J. 265.
13. Iodine Green. Zinc double chloride of chlor-methyl-hexa-methyl-rosaniline-hydrochloride. S. and J. 284.
15. Methylene Green. Nitro tetra-methyl-thionine. S. and J. 349 (foot-note).
18. Aldehyde Green. Quinoline derivative of rosaniline. (?). S. and J. 377.

Natural Colouring Matters.

Wool Book XI.

Lo-kav (on cotton). Chinese dyestuff derived from *Rhamnus utilis*.

CLASS II.—FUGITIVE COLOURS. (WOOL).

Triphenylmethane Colours.

Wool Book XI.

Acid Colours.

1. Light Green SF (yellow shade). Sodium salt of diethyl-dibenzyl-diamido-triphenyl-carbinol-trisulphonic acid. S. and J. 268.
2. Helvetia Green. Sodium salt of tetra-methyl-diamido-tri-phenyl-carbinol-mono-sulphonic acid. S. and J. 266.
3. Light Green SF (blue shade). Sodium salt of dimethyl-dibenzyl-diamido-triphenyl-carbinol-trisulphonic acid. S. and J. 267.
4. Guinea Green BV. Sodium salt of nitro-diethyl-dibenzyl-diamido-triphenyl-carbinol-di-sulphonic acid. S. and J. 270.
5. Guinea Green B. Sodium salt of diethyl-dibenzyl-diamido-triphenyl-carbinol-di-sulphonic acid. S. and J. 269.
9. Fast Green extra. Sodium salt of tetra-methyl-dibenzyl-pseudo-rosaniline-di-sulphonic acid. S. and J. 286.

Basic Colours.—

3. Methyl Green. Zinc double chloride of chlor-methyl-hexa-methyl-*p*-rosaniline-hydro-chloride. S. and J. 283.
4. China Green cryst. Tetra-methyl-diamido-triphenyl-carbinol oxalate. S. and J. 263.
5. Imperial Green cryst. Zinc double chloride of tetra-methyl-diamido-triphenyl-carbinol. S. and J. 263.
6. Solid Green GG. Tetra-methyl-diamido-triphenyl-carbinol-sulphate. S. and J. 263.
9. Solid Green YYO cryst. Zinc double chloride of tetra-ethyl-diamido-triphenyl-carbinol. S. and J. 264.
10. Ethyl Green cryst. Tetra-ethyl-diamido-triphenyl-carbinol-sulphate. S. and J. 264.

Mordant Colours.—

2. Chrome Green (Cr). Tetra-methyl-diamido-triphenyl-carbinol-carboxylic acid.

Safranine and Induline Colours.

Wool Book XI.

Basic Colours.—

17. Azine Green TO. Dimethyl-amido-phenyl-amido-phenyl-pheno-naphthazonium chloride. S. and J. 363.

Azo Colours.

Wool Book XI.

Direct Cotton Colours.—

2. Columbia Green. Constitution not published.

CLASS III.—MODERATELY FAST COLOURS. (WOOL).

Triphenylmethane Colours.

Wool Book IX.

Acid Colours.—

6. Alkali Green. Sodium salt of diphenyl-diamido-triphenyl-carbinol-mono-sulphonic acid. S. and J. 271.
7. Wool Green S. Sodium salt of tetra-methyl-diamido- β -oxy-naphthyl-carbinol-disulphonic acid.
8. Milling Green. Sodium salt of tetra-methyl-dibenzyl-pseudo-rosaniline-disulphonic acid.

Azo Colours.

Wool Book X.

Direct Cotton Colours.—

1. Diamine Green B. From benzidine, *p*-nitro-benzene-azo-amido-naphthol-disulphonic acid, and phenol.

Mordant Colours.—

1. Azo Green (Cr). From *m*-amido-tetra-methyl-*p*-diamido-triphenyl-methane, and salicylic acid. S. and J. 273.

CLASS IV.—FAST COLOURS. (WOOL).

Wool Book X.

Direct Cotton Colours.—

3. Benzo Olive. Constitution not published.

Mordant Colour.—

4. Diamond Green (Cr). Constitution not published.

CLASS V.—VERY FAST COLOURS. (WOOL).

Triphenylmethane Colours.

Wool Book X.

Mordant Colours.—

3. Cœrulein (Cr). Product of the action of sulphuric acid on Gallein. S. and J. 336.

Oxyketone Colours.

Mordant Colours.—

5. Alizarin Green SW (Cr). Sodium bisulphite compounds of tri- and tetra-oxyanthraquinone-quinoline-sulphonic acids. S. and J. 258.

Quinoneoxime Colours.

Mordant Colours.—

6. Dark Green (Fe). Di-quinol-dioxime. S. and J. 232.
7. Gambine Y. (Fe). β -naphtho-quinine- α -oxime. S. and J. 234.
8. Gambine B (Fe). Constitution not published.
9. Naphthol Green B (Fe). Ferrous sodium salt of nitroso- β -naphthol- β -mono-sulphonic acid. S. and J. 236.
10. Dioxine (Fe). β -oxy-naphtho-quinone-oxime. S. and J. 235.
11. Gambine R (Fe). Naphtho-quinone-oxime. S. and J. 233.

NOTES.—The great fastness of the quinone-oxime colours when fixed with iron mordant is worthy of special notice. The fastness of Cœrulein green as a Triphenylmethane Colour is also remarkable, but although Cœrulein is usually classed as a Triphenylmethane Colour, its constitution when fully determined may cause it to be more properly placed in some other class.

SILK PATTERNS.

Most of the foregoing colours were also dyed on silk, and the patterns were exposed to light along with those on wool. The relative fastness of the various colours was, for the most part, the same as on wool, the differences observed being too unimportant to necessitate a special classification for silk.

The Chinese natural dyestuff Lo-kav fixed on silk with alum mordant is much faster than the same colour fixed on cotton from a soap bath. It was not found possible to apply it satisfactorily to wool.

Vat Indigo Blue is apparently less fast on silk than on wool, and on this fibre some of the Alizarin Blues, and notably the Brilliant Alizarin Blues, are much faster than Indigo Blue. As on wool, so on silk, Prussian Blue is faster to light than all other blues.

NOTICES OF BOOKS.

The Development of the Periodic Law. By F. P. VENABLE, Ph.D., F.C.S., Professor in the University of North Carolina. Easton, Pa.: Chemical Publishing Company. 1896. 12mo. Pp. 322.

MANY readers in glancing at the title of this volume will scarcely realise all that the words convey. We may be aware that Mendeleeff and Lothar Meyer have something to do with the periodic system. But what this system includes and involves does not at first sight appear. Before we can have a periodic system, or, indeed, any system, we must have elements; we must enquire into their properties and their mutual relations. We must above all things ascertain their atomic weights, and among all these studies and researches we cannot avoid speculating on their origin. Our author, after quoting the atomic weights as according to Dalton, Wollaston, and Berzelius, enters upon the famous and much discussed hypothesis of Prout. This chemist regarded hydrogen as the primal element with the atomic weight 1, whilst the remaining atomic weights were multiples of that of hydrogen by whole numbers. But the more carefully the atomic weights were determined the more numerous become the cases not to be reconciled with this rule. It was suggested that the half the weight of H ought to be taken as the unit, and Dumas proposed to go further and take as the unit 0.25, *i.e.*, quarter the weight of hydrogen. Still difficulties occurred, and at last the fact remained that the cases where Prout's law proved to be accurate or nearly so were too numerous to be ascribed to chance. The question was raised whether we are not here in presence of a "residual phenomenon," which if eliminated or rightly estimated would justify Prout's law?

Dobereiner's triads was the next suggestion. It was pointed out that there occur analogous elements in groups of three; here the atomic weights of the extreme numbers added together and divided by two gives the atomic weight and the mean. This fact, eloquently elaborated by the great French chemist, J. B. Dumas, at the Ipswich meeting (1851) of the British Association, gave an impulse to the hopes of the transformation of the elements.

Brodie's Ideal Chemistry, sometimes referred to as the "Chemical Calculus," finds here a brief notice.

Perhaps the earliest attempt to devise a systematic and symmetrical arrangement of the whole of the elements is due to M. de Chancourtois, a French engineer. His memoir was presented to the French Academy of Science, and was duly printed in the *Comptes Rendus* for 1862 under the title "Vis tellurique, Classement naturel des Corps simples ou Radicaux obtenu au moyen d'un Systeme de Classification helicoidal et numerique." This paper, although existing in such an influential and accessible form as the *Comptes Rendus*, lay dormant for thirty years, and had absolutely no influence on the development of the periodic theory. Suddenly in 1891 it was disinterred by MM. de Boisbaudran and de Lapparent under the title "Sur une Reclamation de Priorité en faveur de M. de Chancourtois relativement aux Relations numeriques des Poids Atomiques." What was the motive of the authors for keeping silence so long we have neither the right nor the opportunity of inquiring.

J. A. R. Newlands took up the subject immediately after M. de Chancourtois, but quite independently of him. The paper of Newlands when read before the Chemical Society met with a cold, not to say discourteous, reception. Subsequently the question was thoroughly and successfully re-discussed, and the claim of Newlands was vindicated. Our author here writes:—"But none of the savants who entered into the question ever breathed the name of de Chancourtois. His memoirs were at all times accessible in the *Comptes Rendus*. But no one found in them that meaning which MM. de Boisbaudran and Lapparent now assert. Professor Mendeleeff says—

"It is possible that Newlands has prior to me enunciated something similar to the periodic law, but even this cannot be said of Lothar Meyer." Our author, however, makes the bold assertion that "it was impossible for him (Newlands) ever to have developed the periodic law."

The merit of having effected the general recognition of this law is ascribed to Mendeleeff and Lothar Meyer. Which of these two chemists may claim the chief honour Professor Venable does not decide. Mendeleeff considered Carnelley as the only author who had added anything new to it, and denies to Meyer any part in the discovery.

The French, it is remarked, have been especially slow in acknowledging the merits of the discovery, just as in the case of Organic Evolution. Berthelot published an elaborate hostile criticism of the work of Mendeleeff, to which the latter replied in his "Faraday Lecture." Our Royal Society, on the contrary, evaded adjudicating on the respective merit of the Russian and the German chemist by awarding the Davy medal, in duplicate, to both. The position of argon and helium in the periodic scheme has given rise to some new discussion.

The diagram of the elements proposed by Reynolds and modified by Crookes avoids or rectifies some of the manifest defects of the tables of Mendeleeff and Meyer. The lecture on the "Genesis of the Elements," delivered by Mr. Crookes before the Royal Institution, merits more attention than it has received in the work before us.

It is to be remarked that Professor Venable, whilst criticising, and in general fairly, the various theories mentioned, does not give a final summing up, but leaves this delicate task to the reader. It is needless to say that the material with which he has been supplied will prove of incalculable value to the true student of the philosophy of chemistry.

We regret having to notice that the printer uses for the italic *y* and for the Greek *gamma* and *eta* a character which is not practicably distinguishable.

CORRESPONDENCE.

COTTON SEEDS.

To the Editor of the Chemical News.

SIR,—Dr. Wynter Blyth's work on Poisons is so well known, and so highly appreciated by chemists at home and abroad, that Dr. Payne has done well to call attention to an evident mistake with regard to cotton seeds. So far from being a poison, cotton seed, whether whole or decorticated, is one of the most valuable feeding stuffs at the disposal of the farmer, and at the present time cake produced by pressing the decorticated seed is selling at about five shillings per ton more than linseed cake, of which it is stated to be an adulterant.

The imports of cotton seed into the United Kingdom for the past three years have an annual value of over two million pounds sterling, the residual cake from which, after expression of the oil, would all be used for feeding purposes. In addition to this large importation of uncrushed seed there is a large quantity of cake (decorticated, undecorticated, and meal) produced from cotton seeds imported yearly, and classified in the returns as oil cake. Fully half of the imported oil cakes are derived from cotton seed, and the annual value is about £1,000,000. But notwithstanding this large consumption of cotton seed by all kinds of stock, death or injury to cattle or sheep by the use of cotton cake is of rare occurrence, and is chiefly limited to the Brazilian seed or cake, in the latter of which I have frequently found castor seed—a violently poisonous seed—in small proportions.

It seems to me, therefore, highly probable that the cases of poisoning by cotton seed recorded by Dr. Wynter Blyth have been due to a small admixture of some

poisonous seed, such as castor, and not to any poisonous principles in the cotton seed.—I am, &c.,

16, Brunswick Street, Liverpool,
October 19, 1896.

ALFRED SMETHAM.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 15, October 12, 1896.

Thermic Researches on Cyanamide.—Paul Lemoult. —Cyanamide, CNNH_2 , is a very important body on account of its relations with ureas, its constitution, and the numerous products of polymerisation to which it gives rise. It is an endothermic compound, which agrees with its great instability. It is least stable in aqueous solution, in which it behaves as an acid, the energy of which is comparable to that of HCy . It seems, therefore, that the two typical hydrogens of cyanamide are dissimilar. Both can be replaced by monovalent metals, but it is also known that the disodium salt, *e.g.*, if decomposed by water is transformed into a monometallic salt and soda.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. i., No. 9.

Complementary Notes on the Tempering of Steel.—H. M. Have and A. Sauveur.—Translated from the *Journal of the Iron and Steel Institute*.

Manufacture of Alumina at the Works of Larne Harbour.—J. Sutherland.—A translation of a memoir read at a meeting of the Institution of Mechanical Engineers.

MISCELLANEOUS.

Bibliography of Spectroscopy.—At the Liverpool meeting of the British Association (Section B) the Committee on the Bibliography of Spectroscopy presented an interim report to the effect that they had continued and completed the collection and classification of papers on Spectroscopy published up to the end of 1895. They originally intended to bring their work to a close with that date, but asked for reappointment in order that the compilation might be continued to the end of the century. A full report will appear next year.

Detection and Determination of Nitrites in Water.—MM. Barbet and Jaudrier.—A phenylendiamine cannot easily be preserved colourless; the authors, instead, use resorcin in the following manner:—In 2 c.c. of the water to be examined they dissolve 0.1 grm. resorcin in a test-glass, and carefully superstratify upon it 1 c.c. of pure concentrated sulphuric acid. At the surface of contact of the two liquids there appears a colouration which gradually becomes more intense. It is stirred gently to and fro in order not to raise the temperature too much, and after the lapse of an hour the colour produced is compared with that obtained under the same conditions with nitrite solutions of known strength. Water containing only 1/10,000,000 sodium nitrite gives a very characteristic rose colour after the lapse of several hours. —*Journ. Pharm. und Chemie und Chem. Zeitung.*

MEETINGS FOR THE WEEK.

- MONDAY, Nov. 2nd.—Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. "The Production of Inoculating Materials for use in Agriculture (Nitragin)," by Dr. J. A. Voecker, F.I.C. "The Smelting and Refining of Cyanide Bullion," by Arthur Caldecott, F.I.C.
- WEDNESDAY, 4th.—Society of Public Analysts, 8. "Note on Ginger," by Thos. P. Blunt. "Determination of Stearic Acid in Fats," by Otto Hehner and C. A. Mitchell, B.A. "Further Note on Lead in Canadian Cheese," by F. Wallis Stoddart.
- THURSDAY, 5th.—Chemical, 8. "The Constitution of Nitrogen Iodide," by F. D. Chattaway, B.A. "Note on the Solution and Diffusion of certain Metals in Mercury," by Prof. Roberts-Austen, C.B., F.R.S. "Compounds of Metallic Hydroxides with Iodine," by I. Rettie, B.Sc. "The Economical Preparation of Hydroxylamine Sulphate," by E. Divers, M.D., F.R.S., and Tamemasa Haga, D.Sc. "The Reduction of Nitrososulphates," by E. Divers, M.D., F.R.S., and T. Haga, D.Sc. "Amidosulphonic Acid," by E. Divers, M.D., F.R.S., and T. Haga, D.Sc. "The Molecular Conductivity of Amidodulphonic Acid," by Joji Sakurai. "Physiological Action of Amidodulphonic Acid," by Oscar Loew, Ph.D. "Imido-sulphonates—Part II," by E. Divers, M.D., F.R.S., and T. Haga, D.Sc. "How Mercurous and Mercuric Salts change into each other," by Seihachi Hada, B.Sc. "The Effect of Heat on Aqueous Solutions of Chrome Alum," by Margaret D. Dougal. "The Saponification of Ethylic Dicarboxylglutamate," by H. W. Bolam, Ph.D. "The Periodic Law," by R. M. Deely, "The Colouring-matters occurring in British Plants," by A. G. Perkin. "Carbohydrates of Cereal Straws," by C. F. Cross, E. J. Bevan, and Claude Smith.

TO CORRESPONDENTS.

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1928.

ARGON, HELIUM, AND PROUT'S HYPOTHESIS.

By BOHUSLAV BRAUNER, Ph.D., F.C.S.

THE discoverers of argon and helium, and with them the greatest majority of chemists, regard the new gases definitely as new elements, in spite of the fact that the view, according to which they are peculiar, element-like allotropic (polymeric) modifications of nitrogen and hydrogen, possesses many arguments in its favour.

As regards argon, the view that it is N_3 was first pronounced by Dewar, whose view was adopted and defended by new arguments by Mendeleeff, Berthelot, Lothar Meyer, Nasini, the author, and others. As regards helium, the author seems to be the only chemist who regards it as H_3 or H_4 .

The chief argument that argon is a monatomic non-valent new element, with the atomic weight 39.88,—a number which is absolutely incompatible with Mendeleeff's system,—is based on the ratio of specific heats. It should be reminded that first authorities in natural philosophy do not consider the basis of this view, the kinetic theory of gases in its present form, free from objections of a very weighty character, but even, on assuming it to be absolutely correct, it is admitted by several chemists that a highly exothermic, close aggregate of three atoms without internal vibrations—non-valent—possessing only a translatory energy, will behave kinetically like a monatomic gas.

But does the vapour of mercury, the only gas upon which the analogy rests, undoubtedly consist of free single atoms?

It is generally admitted that when a gas possesses two spectra, one of them is due to a disaggregation of its molecules; and until lately this assumption did hold good for mercury, which gives and can give only one kind of spectrum. But since Eder and Valenta have shown that the vapour of mercury gives two kinds of spectra, we must assume that also mercury vapour undergoes a kind of disaggregation, and so the above argument loses much of its weight.

The second argument against argon being regarded as N_3 is, that its density never reaches the number, which would be in this case $d=21.06$. But nowadays, since it is not only probable that argon is a mixture, but a certainty (though the chief constituent largely prevails), the number found, $d=19.94$, must be regarded as a minimum. It has been proved by Kayser beyond all doubt, a year ago, that argon from the air of Bonn contains helium, and this fact was more recently confirmed by Friedländer (*Zeits. Phys. Chem.*, xix., 664) for the air of Berlin. If helium could not be found in English argon by its discoverers, it is easily understood in regard to the fact found by Ramsay and Collie (*Ray Soc.*, Feb. 13), that 33 per cent of helium are invisible in the spectrum of its mixture with argon at 2.62 m.m. pressure. Now argon certainly does not contain such a large amount of helium, and, if the latter became visible to Friedländer, it was only after the greatest part of both gases had been absorbed by the metallic electrodes. Friedländer's view that argon contains only traces of helium seems unfounded, for the author was the first to show (*CHEM. NEWS*, lxxi., 217) how easily helium is absorbed by metallic electrodes, and its relative proportion in Friedländer's argon must have been more considerable, when some of it finally remained unabsorbed.

The recent experiment of Eder and Valenta also made it highly probable that argon is not a homogeneous body,

and the separation of a heavier constituent of $d=20.01$, recently effected by Ramsay and Collie (*CHEM. NEWS*, lxxiv., 25), undoubtedly is an important step towards the higher limit of density.

Supposing for a moment that the hypothesis according to which argon is polymerised nitrogen be correct, we can safely say that no other properties than those of helium may be expected for similarly polymerised hydrogen, so closely is the one problem connected with the other. In helium the metallic properties of hydrogen are more developed than in ordinary hydrogen, for it is not only absorbed by electrodes, but it shows a remarkably high conductivity for electricity (Ramsay and Collie). It is true that, in accordance with the equation $A:N=He:H$, it ought to be more easily condensed than hydrogen, whereas Olszewski tried in vain to condense it at -264° . In the light of the classical experiments of Pictet, who showed that several bodies cannot be insulated against heat rays at low temperatures (solid chloroform fuses again when cooled below its freezing-point), it is not improbable that helium, as a good conductor of heat, is not liquefied at the lowest temperature, not parting so much with its internal energy as is necessary for the assumption of the liquid state.

A study of the specific heat of argon and helium would undoubtedly throw much light on the nature and constitution of these gases. It has been shown by Mendeleeff, in his classical though little-known paper "On the Law of Specific Heat, &c." (*Journ. Russ. Chem. Soc.*, ii., pp. 28 to 46, published in 1870), that, especially for "permanent" gases, the product—

$$\frac{P.c}{n} = 2.4 + \frac{2}{n},$$

where n = number of atoms in a molecule of the weight P —i.e., the atomic heat the more approaches the constant 2.4, the more atoms are contained in a molecule. A determination of the specific heat of argon and helium would probably decide the question whether these gases are monoatomic or polyatomic, for, according to the formula $P.c = n.2.4 + 2$, the molecular heat of argon would possess one of the two values, viz., $P.c=4.4$ for A_1 or 9.2 for N_3 . For helium the values would be $P.c=4.4$ for He_1 , 9.2 for He_2 , 11.6 for H_4 , and 14.0 for H_5 . From this is calculated the specific heat at constant pressure for argon $c=0.110$ or 0.231 , and for helium $c=1.1$ or 3.1 or 2.9 or 2.8 .

Mendeleeff has further shown that the greatest positive difference between the atomic heat—

$$\frac{P.c}{n}$$

as calculated from the specific heat found and between the atomic heat calculated from the formula—

$$\frac{P.c}{n} = 2.4 + \frac{2}{n}$$

appears in the case of gases possessing a higher molecular weight, whereas the greatest negative difference is found in the case of gases, the molecular weight of which is not high when compared with the number of atoms in their molecule, so that gases of a higher molecular weight possess a higher atomic heat.

It is further seen from Mendeleeff's table that, to a certain degree even for gases, the atomic heat is a function of the atomic weight.

If argon and helium are really monoatomic gases, their atomic heat ought to be—

$$\frac{P.c}{n} = 4.4;$$

if they are triatomic, their atomic heat ought to be $= 3.1$.

The values of the specific and atomic heats corresponding to the two alternatives differ so considerably from each other that we may hope that the determination

of the specific heat of the two new gases will throw new light upon the important question whether the gases are mono- or polyatomic, *i. e.*, whether they are new elements or modification of known elements.

The author, for himself, inclines to the view that argon and helium are allotropic states of nitrogen and hydrogen of a peculiar, entirely novel, character. The density of helium, $d=2$, would correspond to a molecular weight = 4, and there would not be a complete analogy between helium and argon, the latter being regarded as N_2 . But the recent classical research of Ramsay and Collie, on the separation of the constituents of helium by diffusion, makes it highly probable that the molecular weights of the two constituents in the pure state are 3 and 5. If there was some possibility of placing *one* helium with a molecular and atomic weight of $He=4$ in the new helium-argon group of the periodic system,* it is impossible, as long as we do not give up the periodic system in its present form (which I would not feel inclined to do), to find a place for two new gaseous, monatomic, and non-valent elements between hydrogen, $H=1$, and lithium, $Li=7$, as well as for $A=40$.

My modest opinion is this, that Nature has effected the synthesis of three substances which behave like elements (or, better, like simple substances, as we speak of molecules), *i. e.*, bodies which it is hitherto impossible to decompose, the molecular, and, with a certain restriction, the "atomic" weights of which equal 3, 5, and 40.† The original protylic matter (in the sense used by Crookes) of the first two element-like substances is hydrogen, and the enormously important bearing of Dr. Ramsay's discovery seems to me to lie in the point that the constituents of helium were formed from hydrogen in accordance with Prout's law.

The final decision of the question on the constitution of argon and helium must be left to the future; and if the author's views on this point differ considerably from those generally adopted, he thinks it more useful for Science to discuss such important, but mysterious, problems as *open questions*, than to adopt prematurely a definite orthodox view.

Bohemian University, Prague,
September 20, 1896.

ESTIMATION OF SULPHUR IN ORES.

RECLAMATION OF PRIORITY.

By Professor L. L. DE KONINCK, University of Liège.

UNDER the above title Mr. J. H. Stansbie indicates as being new the simultaneous employment of nitric acid and bromine for the oxidation of sulphur and sulphides (CHEMICAL NEWS, lxxiv., 189, 1896).

I pointed out this method in 1871 on the occasion of analysing bornite (*Bulletin de l'Académie Royale des Sciences, &c., de Belgique*, 2nd Series, T. 32, No. 11).

I reproduced it in my "Traité de Chimie analytique minérale, qualitative et quantitative," Paris and Liège, 1894, ii., 792.

Far from being new the process is more than a quarter of a century old.

Laboratoires de Chimie Analytique de l'Université de Liège.

* I deny even this, for elements with the atomic weights 4, 20, 38, 82, &c., would have to be placed on ascending parts of Lothar Meyer's curve of atomic volumes, between H and Li, F and Na, Cl and K, Br and Rb, &c., just below the atomic volume maxima, where only elements like the above, possessing the highest amount of energy of the whole period, find their proper places, whereas the atomic volumes of such non-energetic elements as argon and helium must very nearly equal nought. This consideration I regard as one of the most powerful arguments against the view that argon and helium are new elements.

† It will be objected that three atoms of nitrogen and three or five atoms of hydrogen cannot unite according to the "laws of valency." But did protylic matter of which our elements were formed, as admitted by many chemists (a discussion of this question is promised to be held at the British Association Meeting), follow the "laws of valency?"

ON "TWIN-ELEMENTS."*

By RICHARD LORENZ.

(Concluded from p. 212).

The Distribution of all Elements upon the Series of Numbers according to the Geminal Rule.

I WILL now consider the totality of the known elements with reference to their atomic weights and the differences of the latter as regards their distribution along the series of numbers according to the geminal rule.

As the initial point of all the chemical elements we select the atomic weights 3 and 4. These two numbers are to represent the (rounded) atomic weights of elements as yet unknown. They form a pair of twins, and indeed the first. It is named I, twin-pair I = [3, 4]. Here lies perhaps helium, the atomic weight of which is assumed 4.

According to the geminal rule, the round atomic weights of the next following pair of twins must be distinguished from those of the last mentioned by the number 4. We must therefore expect for the next pair of twins the rounded atomic weights [7, 8]. This corresponds to the nearest element known to us, lithium, with the atomic weight 7.03. This consequently occupies in the twin-group the position of the element with an odd atomic weight.

The next following theoretic pair of twins III., must again differ from the foregoing by 4 in its atomic weight. We have to expect [11, 12]. In fact the elements boron and carbon answer this requirement [11.0, 12.003].

It will be perceived that we have passed over glucinium, to which I shall return below. Several such cases will occur.

The following couple of twins, IV., = [15, 16], is not to be found, and in its place stands oxygen with the atomic weight 16.1. It corresponds to the even element of this pair.

We have again passed over an element, nitrogen.

The twin group V. must theoretically consist of elements with the atomic weights [19, 20]. In fact fluorine occupies this position; its atomic weight, 18.99, very close upon 19, causes it to appear as the odd-numbered element of this pair. If the atomic weight of argon is 20, these two elements would be twins.

After fluorine follow sodium and magnesium; in fact they form a twin group (23.058, 24.38), the atomic weights of which correspond to the twin pair VI. = [23, 24].

The following pair [27, 28] corresponds to aluminium and silicon [27.08 and 28.40].

The following elements, phosphorus and sulphur [31.03, 32.063], form the twin pair VIII. = [31, 32].

Twin-pair IX. = [35.36] corresponds to chlorine [35.453].

Then follows the pair X. It is [39.40] = K, Ca = 39.136, 40.

Next we have the twin-pair XI. [43, 44], corresponding to scandium with the atomic weight 44.09. The next twin pair, XII, [47, 48], is titanium, [48.13].

The following twin-couples are recognised as such: XIII., = 51, 52, is formed by [V, Cr = 51.21, 52.15]; XIV. = [55, 56] by [Mn, Fe] = [56.09, 56.0]. The following twin-pair is nickel and cobalt, which, however, is displaced by about one unit from its theoretical value XV. = [59, 60]. On the other hand, we must note that the question as to the magnitude of the atomic weights of both elements is still open. After Krüss had conjectured the presence of an unknown comparison of both elements, Winkler found the atomic weight of cobalt much higher than that of nickel, whilst Hempel and Thiele obtained an inverse result.

The following twin-group, XVI., must have the atomic weights [63, 64]. This is, in fact, represented by copper, with the atomic weights, 63, 64.

The twin-pair XVII. is unknown. But we must remark that zinc ($Zn = 65.38$) is passed over. In like manner the following twin-pair is passed over by gallium ($Ga = 69.9$).

In place of the twin-pair XVIII. = [71, 72] we have germanium (72.32).

Instead of the following twin-pair, XIX. = [75, 76], comes arsenic (75.00). The next twin-group, XX. = [79, 80], is again complete [Se, Br.] = [79.07, 79.963]. The following, XXI. [83, 84], is unknown; the following, XXII. = [87, 88], is represented by strontium, rubidium having been passed over. By overleaping yttrium, zirconium, and niobium, we arrive at the twin-pair XXIV. = [95, 96], in place of which stands molybdenum (96.1). The following twin-pair, XXV. = [99, 100], is not known. If the ekamanganese predicted by Mendeleeff (atomic weight 100) exists, it represents this twin-pair. By passing over ruthenium (101.66) we arrive at rhodium (103.5) which corresponds to the twin-group XXVI. = [103, 104]. In like manner palladium and silver, 106.7, 107.938, represent the next twin group, XXXVII. = [107, 108]. The next metal is cadmium (112.08), which is in the place of the twin-pair XXVIII. = [111, 112]. We must, in passing to the unknown twin-pair XXIX. = [119, 120], overleap indium.

For the twin-pair XXX. = [119, 120] we arrive at [Sn, Sb] = [119.7, 120.29]. The twin-pair XXXI. = [123, 124] is unknown; but the following, XXXII. = [127, 128], is formed by [I, Te] = [126.864, 128], where it requires to be especially noticed that the more probable succession of the two elements I, Te, which cannot be reconciled with the periodic system, is the more probable according to the geminal rule.

With the twin-pair XXXIII. we arrive at a region of elements whose atomic weights are either not accurately known or which follow other laws. These are chiefly the elements of the rare earths, including caesium and barium. Among these the coincidences with the geminal rule are very few. The following are affected:—Caesium, barium, lanthanum, cerium, neodymium, praseodymium, samarium, erbium, decipium, and ytterbium. Some of these elements happen in twin places, but it would be an error to lay any especial weight on this fact.

With the twin-pair XLVI. = [183, 184] a more regular succession commences. It is formed by tantalum and tungsten (182.8, 184.0). The following, XLVII. = [187, 188], is unknown. Of the next, XLVIII. = [191, 192], we know only osmium (191.6); indium, which doubtless belongs here, is at a greater distance ($In = 193.18$). The same relation occurs in the next twin-pair, XLIX. = [195, 196]. Platinum (194.83) forms one of the elements; gold (197.25), which should form the other, is at a greater distance. There follow now only six known metals:— $Hg = 200.4$, $Te = 204.15$, $Pt = 206.911$, $Bi = 209.0$, $Th = 232.4$, $U = 239.4$. All these fall at the places required by the geminal law. Mercury represents the twin-pair L. = [199, 200], thallium the twin-pair LI. = [203, 204], lead and bismuth LII. = [207, 208], thorium LVIII. = [231, 232], uranium LX. [239, 240]. It must be a surprise that lastly elements of such high atomic weight lie at the places theoretically required with the same distinctness as the earlier elements.

I may now sum up the results. The following elements, in the first place, follow the geminal rule:—He (?), Li, B, C, O, F, Ar (?), Na, Mg, Al, S, P, Si, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Ge, As, Se, Br, Sr, Mo, R, Pa, Ag, Cd, Sn, Sb, I, Te. In opposition to this extremely long series of thirty-nine elements, with atomic weights of from 4 to 128, there are only ten exceptions:—H, Br, N, Zn, Ga, Rb, Y, Zr, Nb, In.

In the following part of the series the exceptions increase, especially as regards the rare earths. But even here the best known elements, and those most frequently examined, follow the geminal rule. This is verified by Ta, W, Os, Pt, Hg, Tl, Pb, Bi, Th, U, whilst Cs, Ba, Ir, Au, form important exceptions.

In the remaining elements, La, Ce, W, Pr, Sa, Er, Dy, Yb, we find some agreements and some exceptions, but these may be disregarded.

On the whole the following elements follow the geminal rules:—Helium (?), lithium, boron, carbon, oxygen, fluorine, argon (?), sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, scandium, titanium, vanadium, chromium, manganese, iron, nickel, cobalt, copper, germanium, arsenic, selenium, bromine, strontium, molybdenum, rhodium, palladium, silver, cadmium, tin, antimony, iodine, tellurium, cerium, iridium, decipium, tantalum, tungsten, osmium, platinum, mercury, thallium, lead, bismuth, thorium, uranium.

A final decision cannot be pronounced concerning those elements which, according to our present knowledge, do not agree with the regularity here discussed. It is possible that a certain part would fall in on a revision of their atomic weights. This might be especially expected in case of those elements which already approach very closely to their theoretical places. Thus lanthanum (138.5) is very near the theoretical value 139, which would form a twin-pair with cerium (140.2). The atomic weight of lanthanum is not accurately determined; the fourth place is uncertain, and a displacement of a few tenths would bring lanthanum so near to cerium as to form a twin-pair. The case is very different where elements with well-determined atomic weights do not adapt themselves to the geminal rule. Exceptions like glucinum, nitrogen, zinc, barium, gold, &c., are very important, and for the present tell in any case against the universality of the geminal rule. But it is to be remarked that the number of exceptions is small as compared to the coincidences. Nothing compels us to assume that all the elements must follow the geminal rule. The elements may be built up in the manner of the hydrocarbons. In these the molecular weights vary by a constant difference on the access of one and the same group, $e.g., = CH_2$. If we assume this as possible for an element, it is conceivable that a series of other elements might be built up on a different plan.

LABORATORY LAYS.

By H. B.

To be placed amid smoking chimneys and compelled to spend month after month determining the same element in similar material is a necessity dire enough to hatch anything. The apparatus described in *CHEMICAL NEWS* (vol. lxxiv., p. 63) was devised to relieve a monotony, and at the same time to provide a little leisure which might be more pleasurably employed.

The modified form of an aspirator, to be described, is similarly less troublesome, and more desirable in point of accuracy than the form ordinarily employed. The principle is certainly not new, but so far as I know—and I have looked through all handy catalogues, text-books, &c.,—it has never been applied to an aspirator. In case I have been anticipated the arrangement is certainly not well known, and yet so simple and effective withal that it will bear reproduction.

During combustion a furnace tube is usually aspirated by allowing water to run from an attached bottle either clean away or into another bottle, which afterwards takes the place of the former.

The object of aspirating is to preserve the gas in the heated tube at a pressure slightly less than that of the atmosphere, so that in case a slight leak is developed the air may be drawn in rather than the contained gases or vapours pass out. When an ordinary form of gasometer is employed along with the customary aspirator, the pressure in the tube will depend on the head of water in the upper portion of the gasometer and the height of

water to be run out in the aspirator; both these are decreasing forces, and if they act as they should at any one time, they are gradually growing weaker and weaker, and must either be readjusted time after time or permitted to act indifferently.

The apparatus shown in the figure avoid these shortcomings.* It needs no explanation, though it may be advisable to show why the suction is always constant. The tap of the tubulure having been opened the water issues from c. Through the tube P (imagine it detached from the KHO bulb) only can the air reach the inside of the bottle. The dribbling of the water from c causing the suction depends on—

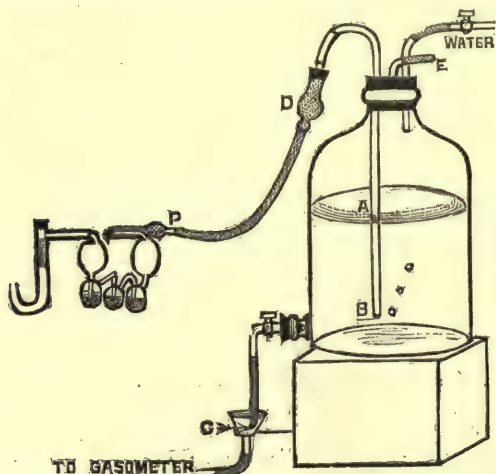
Forces pushing water out of c are—

Weight of column of water AC + (pressure of the atmosphere less weight of column AB on the water in the bottle); that is the pressure of the atmosphere—weight column BC.

Force pushing water back at c is—

Pressure of the atmosphere.

The resultant of these forces is the weight of the column BC acting downwards, and this is constant so long as B dips in the water. The length BC is adjusted so that when P is attached to the KHO bulb the air can just be pulled through the purifying train, furnace, &c.



The water from c drops in the funnel, and is conveyed to the water hold of the gasometer, which stands in a cupboard underneath. If there were no combination of oxygen with carbon and no consequent absorption of CO_2 in the KHO, the water in the hold would preserve its level. As it is, however, it does not vary appreciably during a combustion, and very little during the consumption of the gasometer full of O.

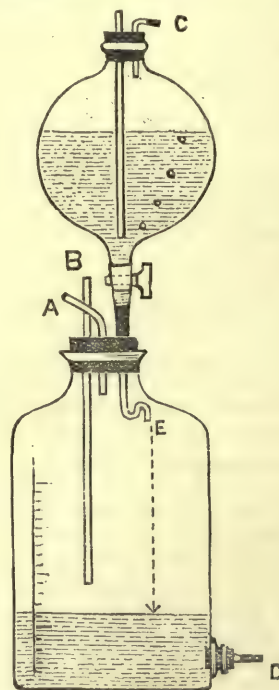
D is filled with CaCl_2 . The bottle is re-filled directly from a tap, and at these times the tubulure tap is closed, and the rubber cap E removed so that the displaced air may escape. When not in use either the tubulure tap or the tube E must be open, otherwise the water may rise in the tube and spoil the CaCl_2 .

Gas Extinguisher.

When the carbonaceous matter from a steel has been transferred to a boat it is dried in a water oven for two or three hours. It sometimes happens that they are boated just before leaving for the day, and must be burned first thing on the morrow. An arrangement for turning out the gas after a given number of hours is reproduced in CHEMICAL NEWS, lxiv., 202, from a description in the

Chemiker Zeitung, omitting, however, two very important particulars, viz., a perfectly constant water flow, and a means of preventing gas escape when the cistern is empty. An arrangement supplying these necessary features is the excuse to be offered for this note.

In the figure gas enters through A and leaves through B (which moves through the stopper). As soon as the water dropping from E raises the level to the lower end of B the flame is extinguished. The separatory funnel is fitted according to the principle of the preceding aspirator. The lower bottle is graduated, or the graduation may be on the movable tube B. The volume of 100 drops from the jet E is measured and marked on the bottle. If now the drops are arranged to fall at so many per minute, the volume falling in any time can be readily calculated, and the sliding tube B adjusted accordingly. The stoppers must of course be air-tight, and that being once fitted they need not again be removed—C and D are inserted so that the vessels may be respectively filled and emptied. The whole arrangement rests on a retort stand with the



ring under the funnel. The funnel may be replaced by another aspirator bottle; such an arrangement in two trials made during the day acted in sixty-two minutes and four-and-a-quarter hours when set for sixty-one minutes and four hours respectively.

Filtration.

A great number of experiments have been made to shorten filtering operations. Asbestos felt supported on a perforated disc in a funnel throat is always used where possible. By this means finely divided precipitate which need repeated filtering through paper are readily disposed of, but it must be noted that with very fine precipitates, when once the filtration is begun, the funnel must not be allowed to run dry or the process stopped in any other way. Neglect of this precaution often allows the precipitate to pass through. Even if the filtration be stopped by placing the finger over the end of the funnel stem the precipitate will run through when the filtration is continued. In dark coloured solutions this point may be easily overlooked, and low carbon percentages in much

* This is not quite true of an ordinary gasometer, because the tube supplying water from the upper hold passes below the water level in the gas hold. An obvious alteration would amend this.

worked tungsten and chromium steels are often due to no other cause than this.

Asbestos may be very conveniently replaced by paper pulp, made from the clippings of soft ashless filter-paper. These devices had been used long before the admirable papers of Casamajor (*CHEMICAL NEWS*, xlv., 8; xxxii., 33) were seen. The paper pulp filter has been much used for separating the manganese oxide after precipitation with Br and Am. The compact precipitate is not brought on to the filter until last. Having sucked the filter dry it may readily be transferred to a crucible as follows:—Lift the edge of the felt with a forcep leg, then grasp it by its clean underside and lift it boldly into the crucible. A piece of moistened filter-paper, about three-quarters of an inch square, laid on the first finger and pressed from the neck to the rim, the other hand meanwhile turning the stem, makes the funnel perfectly clean and involves less trouble than the truncated filter-paper proposed by Casamajor. Unless the felt is laid rather thick or sucked hard, thus more or less impeding the filtration, the impact of the liquid on the new filter disturbs the pulp, and may cause a little precipitate to pass through. This may be obviated by laying a piece of filter-paper the size of a six-penny piece, on the centre of the pulp, and allowing the liquid to strike it. Our experience with felts has led us to adopt them only when the precipitate is crystalline and open, or needs little or no washing.

The rapid filtration is largely due to the power the felt has of holding the funnel stem full of water. An ordinary filter-paper acts better when this condition obtains, but it is not always, even when intended, that this happens. With small filters the following plan acts well. Fit and wet the paper as usual, then draw the paper bodily for a little way up one side of the funnel, having previously stopped the stem with the finger. When the stem has filled with water push the paper down again and remove the finger. The column of water is invariably held with a smooth funnel; a fluted one is not so certain.

Sheffield.

THE SEPARATION AND IDENTIFICATION OF POTASSIUM AND SODIUM.*

By D. ALBERT KREIDER and J. E. BRECKENRIDGE.

THE application of the spectroscope to the detection of potassium and sodium, for which there has thus far been no alternative, is not so unsatisfactory in the evidence as to the presence or absence of these elements as it is in its utter failure, except under delicate quantitative comparisons, to give any idea as to the quantity of either element indicated; and since the most minute quantity of either element is sufficient to produce its characteristic line in the spectroscope, together with the fact that so many of the reagents employed in analysis contain a trace of alkali, the indication of the spectroscope is rendered misleading. While to the careful observer the presence or absence of potassium is invariably revealed, all evidence as to the ubiquitous element sodium is practically worthless. It has, therefore, appeared advisable to us to undertake the following work looking toward a method for the direct determination of sodium based upon the principle of the perchlorate method for the quantitative determination of potassium. The fact that, in the form of the perchlorate, potassium is insoluble while sodium is readily soluble in 97 per cent alcohol, affords a means for the separation of the two elements as well as for the identification of the former. By converting the sodium in the filtrate from the precipitated potassium salt either to the chloride or sulphate, in which forms it is insoluble in alcohol, a means for the detection of sodium is also provided.

Assured by the experiments previously published by one of us (Kreider, *Amer. Jour. Sci.*, xlix., 448), that the determination of potassium according to this method would be sufficiently accurate, our experimentation was directed towards determining the conditions of greatest utility and delicacy for the detection of sodium. In converting the sodium from the perchlorate to the chloride, attempts were first made to substitute some soluble chloride for the free acid, the addition of which to the alcoholic solution of sodium perchlorate it was feared might result in the formation of the dangerously explosive compound, perchloric ether. But aniline hydrochloride, prepared by saturating a solution of aniline in absolute alcohol with gaseous hydrochloric acid, when applied to the precipitation of 0.010 gm. of sodium perchlorate dissolved in 5 c.m.³ of 97 per cent alcohol, proved so hopelessly inadequate that we resorted immediately to the use of free acid, which, fortunately, was found perfectly safe even in the presence of considerable perchloric acid and at the boiling point of the mixture.

The strongest aqueous solution of hydrochloric acid, however, is inapplicable, as was proved by several experiments in which as much as 0.010 gm. of sodium perchlorate, dissolved in only 5 c.m.³ of 97 per cent alcohol, failed to be revealed by the addition of the strongest aqueous solution of the acid, added in quantities varying from a single drop to 10 c.m.³—not the slightest turbidity being produced. By substituting for the aqueous solution for the acid, a saturated solution of hydrochloric acid in 97 per cent alcohol, of which 5 c.m.³ were used for the precipitation, quantities of from 0.002 to 0.003 gm. of sodium perchlorate dissolved in 5 c.m.³ of 97 per cent alcohol could be detected with certainty; but this could not be made sufficiently delicate. Concentrated sulphuric acid was also applied as the precipitant, and was found reliable for quantities of about 0.003 gm. of sodium perchlorate dissolved in 10 c.m.³ of 97 per cent alcohol, when a single drop of the acid was added, but an excess of the acid caused the precipitate to re-dissolve. Gaseous hydrochloric acid proved most effectual. The dehydrating effect of the acid upon the alcohol greatly increases the insolubility of sodium and secures a remarkable delicacy, as is evident from the results recorded in Table I.

TABLE I.

NaClO ₄ taken.	Na ₂ O equivalent.	97 per cent. alcohol.	Indication.
Grm.	Grm.	C.m. ³ .	
0.0100	0.00250	10	very strong
0.0050	0.00125	10	strong
0.0040	0.00100	10	"
0.0030	0.00075	10	"
0.0030	0.00075	10	good
0.0020	0.00050	10	"
0.0020	0.00050	10	"
0.0010	0.00025	10	"
0.0005	0.00012	10	trace
0.0003	0.00006	10	"
0.0001	0.00003	10	none
0.0000	0.00000	10	"
0.0010	0.00025	40	distinct

The sodium employed in these determinations was in the form of perchlorate, prepared by evaporating sodium chloride, free of potassium and ammonium, with perchloric acid until tests for hydrochloric acid proved a complete conversion to the perchlorate, when the excess of acid was volatilised by heating over a drying cone. Two grms. of this purified salt were dissolved in 200 c.m.³ of 97 per cent alcohol, and served for our standard solution for those tests in which quantities greater than 0.001 gm. of sodium perchlorate were used. When it appeared evident that smaller quantities could be detected with certainty, a solution of the salt containing 0.050 gm. per 100 c.m.³ of water was used, and each portion evaporated to dryness before adding the alcohol. In each case the alcohol subsequent to its addition was saturated

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. ii., Fourth Series, October, 1896.

with gaseous hydrochloric acid, being kept cool by immersion in a beaker of water. For the generation of hydrochloric acid, the well known form of apparatus consisting of a side neck flask, containing sodium chloride covered with hydrochloric acid fitted with a stoppered funnel, through which sulphuric acid could be admitted as desired, served admirably.

It is evident, then, that by the use of 10 c.m.³ of 97 per cent alcohol with gaseous hydrochloric acid 0.0003 grm. of sodium oxide can be found with certainty; and when the alcohol is allowed to become saturated with the gas even 0.0006 grm. of sodium oxide will be unmistakably revealed. The quantity of alcohol, 10 c.m.³, is sufficient for all purposes, since this amount will dissolve about 2 grms. of sodium perchlorate; but even in 40 c.m.³ 0.0002 grm. of sodium oxide may be seen distinctly; from which fact it is evident that this method can be applied to the quantitative determination of sodium. Absolute alcohol does not materially increase the delicacy of the test.

In Table II, are recorded the results of experiments made upon mixtures of the two elements. The sodium and potassium taken were drawn from separate standard solutions containing 1 grm. of the purified perchlorates in 100 c.m.³ of distilled water. After evaporating to dryness on the steam bath, the residue was treated with the usual amount of 97 per cent alcohol, the insoluble potassium perchlorate was removed by filtering through a dry paper filter and dry funnel into a dry test tube, and the filtrate saturated with gaseous hydrochloric acid.

TABLE II.

KClO ₄ taken. Grm.	K ₂ O equivalent. Grm.	NaClO ₄ taken. Grm.	Na ₂ O equivalent. Grm.	Indication for potassium. strong	Indication for sodium. strong
0.0500	0.01699	0.0500	0.01250		
0.0200	0.00680	0.0200	0.00500	"	"
0.0100	0.00340	0.0100	0.00250	"	"
0.0050	0.00170	0.0050	0.00125	"	"
0.0040	0.00136	0.0040	0.00100	good	good
0.0030	0.00102	0.0030	0.00075	"	"
0.0020	0.00068	0.0020	0.00050	"	"
0.0010	0.00034	0.0010	0.00025	"	"
0.0005	0.00017	0.0005	0.00012	trace	trace
0.0003	0.00010	0.0003	0.00007	"	"
0.0001	0.00003	0.0001	0.00003	faintest trace	none
0.0000	0.00000	0.0100	0.00250	none	strong
0.0100	0.00340	0.0000	0.00000	strong	none

These results prove that the two elements when combined in any proportion may be separated and identified with great delicacy.

Before applying this method, however, it is necessary to remove certain interfering substances. While potassium may be safely tested for in the presence of other bases and acids, except ammonium, cesium and rubidium, and sulphuric acid (*loc. cit.*), the large number of elements whose chlorides are insoluble in alcohol necessitates their removal before testing for sodium. But among the common alkalis ammonium is the only one whose presence is objectionable. Lithium does not affect either the test for potassium or sodium, as was determined by an experiment in which about 0.1 grm. of lithium chloride was converted into the perchlorate by evaporating with an excess of perchloric acid and treated with 10 c.m.³ of 97 per cent alcohol. A perfectly clear solution was obtained, which upon saturation with gaseous hydrochloric acid and cooling, remained clear. The removal of sulphuric acid is necessitated by the insolubility of sodium sulphate in alcohol.

TABLE III.

Bases taken. Pb, Cu, Al, Fe, Zn, Ba, Ca, and Mg. as nitrates. Grm.	K ₂ O taken. Grm.	Na ₂ O taken. Grm.	Indication for potassium.	Indication for sodium.
0.0500 of each	0.0000	0.0000	faintest trace	trace
0.0500 "	0.0017	0.0012	good	good
0.1000 "	0.0000	0.0000	faintest trace	trace
0.1000 "	0.0000	0.0005	"	good

In the experiments made with potassium and sodium associated with other acids and bases, the results of which are recorded in Table III., the following treatment was adopted. The several groups of bases were successively removed in the ordinary way: Hydrogen sulphide in ammoniacal solution removed the lead, mercury, copper, and zinc. Barium and calcium were removed by ammonium carbonate, the final filtrate being evaporated and ignited to the complete volatilisation of ammonia. The residue was dissolved and treated with barium hydrate for the removal of magnesium, and after filtering the barium was again removed by ammonium carbonate and the filtrate evaporated and ignited as before. This residue was then treated with 10 c.m.³ of boiling water, and after stirring was filtered in order to remove the organic matter usually found at this stage of the treatment. To the filtrate was added 0.1 to 0.5 c.m.³ of pure perchloric acid, about 1.7 sp. gr., according to the amount of residue, and evaporated over the steam bath until the white fumes of perchloric acid appeared. When the quantity of sodium is large it is safer to evaporate several times in order to secure a complete conversion to the perchlorate, and in such case precautions must be taken to have sufficient of the acid present. Upon treating with 97 per cent alcohol the presence of potassium is revealed by an insoluble residue. This is removed by a dry filter, and the filtrate saturated with gaseous hydrochloric acid, whereupon sodium, if originally present in amount greater than 0.0005 grm. of the oxide, will be precipitated in granular condition.

The fact that minute traces of sodium and potassium are found in the blank tests is to be expected from the delicacy of the method as proved by Tables I. and II., when it is remembered that but very few of the so-called chemically pure reagents are absolutely free of sodium, and that even distilled water kept in glass vessels contains a trace of the alkaline elements. However, the indication for sodium in the blank tests appeared only as a cloudiness, and after complete saturation, while even the quantity of sodium oxide present is not less than 0.0005, the precipitate appears in granular form and before the alcohol is completely saturated, which leaves the method all that could be desired for qualitative determinations.

Preparation of the Perchloric Acid.—The perchloric acid prepared according to the method previously published by one of us (Kreider, *Amer. Jour. Sci.*, xlix., 443), by converting sodium chlorate into the perchlorate by heat, destroying the residual chlorate by treating with the strongest hydrochloric acid, from which the sodium chloride was separated by filtering through a Gooch filter and the excess of hydrochloric acid removed by evaporation—while answering perfectly well for the detection of potassium, is inapplicable to the test for sodium, because of the small amount of this element which the acid always contains, due to the partial solubility of sodium chloride in hydrochloric acid. As distillation seems the only method for the removal of this residual sodium, our attention was given to a study of the best conditions for the distillation. Various experiments led to the adoption of the following treatment, which we found in every case perfectly safe and fairly rapid. To prevent loss by decomposition the distillation must be carried on under diminished pressure, and unless the acid has been previously concentrated by evaporating until the white fumes appear, if there is any considerable amount of the acid in the distilling flask, even with porcelain chips to check it, it bumps with such violence as to throw the liquid to all parts of the flask and possibly into the condenser. It appeared to be essential, therefore, to start with only a small amount of the concentrated acid in an apparatus which would permit of the gradual addition of the acid without relieving the vacuum. Rubber stoppers or connectors are not advisably used where the acid may condense upon them and flow back into the flask. Invariably oxidisable matter is carried back, causing explosions

which vary in force and seriousness according to circumstances.

We, therefore, selected a strong distilling flask of about 100 c.m.³ capacity, and sealed into the tubulation a stoppered funnel which reached well into the bulb. The stop-cock of this funnel was carefully cleansed of vaseline and lubricated with metaphosphoric acid obtained by boiling syrupy orthophosphoric acid until the temperature of 350° C. has been attained.* The side neck of the flask was inclined upward for a short distance before being bent into the receiver, with which it was connected by a rubber stopper through which the tube extended for a safe distance. An ordinary bottle of 250 c.m.³ capacity served for a receiver, and was closed by a doubly perforated stopper. Through one of the perforations the adapter from the condenser was entered; through the other connection was made with a small glass bulb inserted between the receiver and the next tube, containing moistened sticks of caustic potash, in order to prevent the potash from reaching the receiver in case of an accident to the pump. The object of the potash was to absorb any chlorine resulting from the inevitable slight decomposition of the acid, and thus to protect the mercury of the pump. For the exhaustion an automatic pump was employed, and generally twenty minutes would suffice to reduce the pressure to about 8 m.m., when the distillation was begun. The pump gradually reduced the pressure, which was kept at about 3 to 5 m.m. The bottom of the distilling flask was covered with a layer of fine porcelain chips to a depth of about 1 c.m., and the whole flask was surrounded by a cylinder of thin sheet iron closed below, while the upper opening was protected by an asbestos cover. By this means heat was uniformly applied to every part of the flask and up to the point at which, if the acid condensed, it would flow into the receiver. Three or 4 c.m.³ of the acid were admitted to the flask, after which the temperature was raised to about 130° C. and the acid admitted at about the same rate that it dropped from the condenser, care being taken to prevent the liquid in the distilling flask from disappearing entirely. No danger was experienced in admitting the acid; the porcelain chips distribute the heat and prevent the colder acid from reaching the glass.

Careful compliance with the above conditions will secure satisfactory results. As a rule we succeeded in distilling at the rate of 25 c.m.³ to 40 c.m.³ per hour, and when it is remembered that the product is the dihydrate of perchloric acid, the most concentrated form in which it is stable, and of which 0.1 gm. of potassium oxide requires only 0.16 c.m.³, it will be seen that by this process the acid may be prepared without great difficulty.

DETERMINATION OF URIC ACID IN GUANO.†

By A. STUTZER and A. KARLOWA.

For a long time past guano imported from Peru has been comparatively poor in uric acid; of late, however, cargoes have arrived equalling in quality the best shipped during the fifties; the determination of the quantity of uric acid present in these new shipments is, therefore, of some interest. We endeavoured to find a method for its determination, and the following seemed likely to be suitable.

A good average sample of the guano is reduced to fine powder and, if rich in nitrogen, 1 gm., or if poor, 2 grms., taken for the determination. This is placed in a porcelain basin, some water added, and then

hydrochloric acid to slight acid reaction. The liquid is evaporated on the water-bath until all hydrochloric acid is expelled, 100 c.c. of water, containing 3 grms. of piperazine in solution, added, and the whole boiled for about a minute. It is then filtered, cooled, a little phenolphthalein added, and just sufficient hydrochloric acid to correct the alkaline reaction; 10 c.c. of a 10 per cent hydrochloric acid solution are now added, the solution well stirred (preferably by the aid of a stirring machine), and allowed to stand for 12 hours. The separated crystals of uric acid are collected upon a filter of known (but lowest possible) percentage of nitrogen, and washed with water containing 1 per cent hydrochloric acid, until the filtrate and washings together amount to 200 c.c. With the filter and its contents a nitrogen determination is made, and the percentage of uric acid calculated from the nitrogen found, 1 part being equal to 2.994 parts uric acid.

It was necessary, however, in the first place to determine the solubility of uric acid in a 1 per cent hydrochloric acid solution, in order to establish the proper correction for solubility. We obtained for this purpose a specimen of the purest commercial uric acid—a fine white powder—and found that 100 c.c. of the 1 per cent hydrochloric acid solution were capable of dissolving at the mean temperature of the room 0.0084 gm. uric acid, an amount represented by the proportion 1:11890. We obtained quite different figures, however, on experimenting with uric acid in the crystalline state. Some uric acid was dissolved in piperazine, separated, as before described, with hydrochloric acid, filtered after standing for twenty-four hours, washed with water, and dried at 100° C. The analysis showed 33.30 per cent nitrogen, as against 33.31 per cent required by theory. Determinations made with this preparation showed that it dissolved with much greater difficulty, only 1 part in 43,478. The 100 c.c. dissolved 0.0023 gm. We are only able to explain this difference by attributing it to the crystalline structure of the uric acid, for as the commercial specimen first used was also pure according to chemical analysis, the only difference between the two preparations was that of physical character.

In making use of this method we have to calculate the solubility upon 200 c.c. of filtrate. It is, however, only the first 100 c.c. that can be considered as saturated with uric acid; the washings contain less. If, therefore, we assume that the 200 c.c. of filtrate and washings contain 0.003 gm. uric acid, and we add this amount to the results obtained, we make the nearest approximation to the truth.

We found in a sample of Chinchas Peruvian guano, imported by the Anglo Continental Guano Works, Hamburg, 27.60 per cent uric acid, other constituents of manurial value being also present, as follows:—

Phosphoric acid soluble in citrate by P.	
Wagner's method	9.25 per cent
Total phosphoric acid	9.60 "
Nitrogen in the form of uric acid	9.20 "
Nitrogen in other organic forms	4.00 "
Nitrogen in the form of ammonia	2.10 "
Total nitrogen	15.30 "

In another sample of Chinchas guano we found 23.82 per cent uric acid and the following other manurial constituents:—

Phosphoric acid soluble in water	3.32 per cent
Phosphoric acid soluble in citrate by Wagner's method (which includes that soluble in water)	8.54 "
Total phosphoric acid	10.37 "
Potash	2.41 "
Nitrogen in the form of uric acid	7.96 "
Nitrogen in other organic forms	4.21 "
Nitrogen in the form of ammonia	2.30 "
Total nitrogen	14.47 "

* This lubricant will be found entirely satisfactory and greatly preferable to vaseline in many other operations where the greasy effect of the latter is objectionable.

† *Chemiker Zeitung*, xx., 721.

The quantity of uric acid present in these guanos is noteworthy. Whether the method used for its determination would also be suitable for the analysis of other substances we have not yet ascertained.

NOTE ON USE OF GEISSLER FILTER-PUMP AS AN ASPIRATOR.

By E. G. BYRANT.

THE glass pump is connected to a water tap as usual, the suction tube being attached to any apparatus through which a current of air is required. The current can be thus easily made continuous and of any desired rapidity. Moreover, by means of a short piece of indiarubber tubing at the bottom of the pump, specimens of the aspirated air can be collected at a pneumatic trough provided with overflow.

THE PRESENCE OF NITRITES IN THE AIR.*

By GEORGE DEFREN, M.S.

It is well known that the atmospheric air contains, besides its main normal constituents, oxygen and nitrogen, admixtures in varying quantities of not only carbon dioxide and aqueous vapour, but, especially in the neighbourhood of cities (Mabery and Snyder, *Journ. Am. Chem. Soc.*, xvii., 105), ammonia and various gases arising from industrial processes and resulting from the decomposition of animal and vegetable life.

The amounts of the impurities in the air may be very small. Ammonia exists sometimes to the extent of one part in 1,000,000. Ozone is said to be produced by electrical discharges during storms, by the breaking of waves on rocks, and other causes (Gorup V. Besanez, *Ann. Chem. Pharm.*, clxi., 232). It has been shown (Carius, *Ber. Deut. Chem. Gesell.*, viii., 1481) that when ammonia and ozone unite in the air they form hydrogen peroxide, ammonium nitrite, and ammonium nitrate. It has also been observed (Goppelsroder, *Jour. f. Prakt. Chem.* [2], iv., 139, 383; Smith "On Air and Rain," 438; Bechi, *Ber. Deut. Chem. Gesell.*, viii., 1203) that rain obtained during thunder-storms contained more nitrites and nitrates than ordinary rain, from which we conclude that electrical discharges have some effect on this combination.

Aside from the above several investigations have been carried out to determine the origin of nitrites in the air and the possible effect of these nitrites on the human system. Boke (*CHEM. NEWS*, xxii., 57) claims that when illuminating gas is burned the higher oxides of nitrogen are formed. W. V. Hoffmann (*Ber. Deut. Chem. Gesell.*, 1870, 658) noticed that on combustion a gas was formed which had a reddish colour and possessed an odour resembling that of nitrous acid. E. A. Greeve and P. Zoeller showed (*Ber. Deut. Chem. Gesell.*, 1877, 2144 b), by a conclusive investigation, that when absolutely pure hydrogen was burned in pure air the condensed water formed showed an appreciable quantity of nitrous acid by the use of Griess's reagent. Berthelot (*Comptes Rendus*, lxxxix, 882) and Stohmann (*Jour. f. Prakt. Chem.*, xix., 142) found that by the combustion of nitrogenous bodies nitrous, nitric, and hyponitrous acids were formed. Leens (*Am. Chem. Soc. J.*, 1884, 3), Wurster (*Ber. Deut. Chem. Gesell.*, 1886, 3202, 3206), and Wright (*Chem. Soc. J.*, xxxvii., 422; *CHEM. NEWS*, xli., 169; *Chem. Ind.*, 1880, 207) also found nitrous acid as a product of the combustion of illuminating gas. Louis Ilosvay de N. Ilosva (*Bull. Soc. Chem. d. Par.*, 1889, ii., 377; *Ber. Deut. Chem. Gesell.*, 1889, 793) made extensive researches on the subject, and came to the conclusion that the higher oxides of nitrogen were formed, but that no ozone nor hydrogen peroxide could be obtained. The presence of hydrogen peroxide

in snow and rain (Schöne, *Ber. Deut. Chem. Gesell.*, vii., 1695) was due to other causes. Finally, Alfred Von Bibra (*Archiv f. Hygiene*, xv., 216) investigated the question, and obtained considerable nitrous acid when illuminating gas was burned. Mabery and Snyder (*Jour. Am. Chem. Soc.*, xvii., 121) have recently determined the amounts of nitrites found in air in various localities.

That headache and depression are experienced in crowded rooms is universally recognised, but the exact cause is not yet clearly determined. Formerly the presence of excessive carbon dioxide was supposed to be sufficient to account for the evil effects of bad air, but the researches of Hammond, Brown-Sequard, and D'Arsonval (*Comptes Rendus*, 1888, 33; *Société de Biol.*, 99, 99, 108, 110), and Merkel (*Archiv f. Hygiene*, xv., 1), claim the presence of a volatile organic poison in the fluid condensed from expired air. The results, however, have been contested by Dostre and Loyer (*Comptes Rendus*, lxxxviii., 91—99), Russo Gilbert and Alessi (*Boletino della Società d'Igiene di Palermo*, lxxxviii., Nr. 9), Hofmann-Wellenhof (*Wiener Klinische Wochenschrift*, lxxxviii., Nr. 37), Lehmann and Jessen, (*Archiv f. Hygiene*, x., 267), Bergey, Mitchell, and Billings ("Report to Smithsonian Institution"; *Nat. Acad. Science*, April 16, 1895; *Science*, New Series, i., 481, 482). The latter-named investigators claim that the injurious effects of air expired from the lungs appear to be due entirely to the diminution of oxygen or increase in carbon dioxide, or to a combination of these two factors, and state that it is improbable that the minute quantity of organic matter contained in expired air has any deleterious influence on men who inhale it in crowded rooms.

Even if no organic poison be exhaled from the lungs it is nevertheless a fact (Merkel, *loc. cit.*) that mice placed in closed receptacles and forced to breathe the expired air from other mice quickly died, showing the presence of some harmful substance. In direct connection with this observation stand the results obtained by Falck (*Lehrbuch d. Prakt. Toxicologie*, 1880, S. 64), Husemann (*Lehrbuch d. Toxicologie*, Chazier (*Bull. de la Soc. Med. d'Emulat.*, 1823), Sucquet (*Jour. d. Med.*, 1860), Desgranges (*Jour. d. Med.*, T. 8), Eulenberg (*Die Lehre von d. gift Gasen*, 1865, 251), Purcell (*Med. and Surg. Report*, 1872, p. 313), Schmitz (*Berl. kl. W. Schr.*, 1883, S. 428; 1884, S. 335), and Pott (*D. Med. Woch.*, 1884, 29, 30), on the poisonous qualities of nitrous acid.

With the more delicate methods of determining nitrites it has been proved that they exist in the air of inhabited rooms: hence the question naturally arises, Could the presence of nitrites in the air exert any influence in causing the effects hitherto wholly attributed to the carbonic acid gas? Ilosvay (*loc. cit.*, *Ber.*, 798 c.; *Bull. Soc. Chem.*, 388—391) claims that nitrites are exhaled from the lungs, and Wurster (*Ber. Deut. Chem. Gesell.*, 1886, 3202, 3206) and Cramer (*Jour. f. Gasbeleucht u. Wasserversorg.*, 1891, 65; *Archiv f. Hygiene*, 10, 321) maintain that the nitrites formed by the combustion of illuminating gas are the direct cause of the depressed feeling and uneasiness experienced in crowded rooms, while Rübner shows (*Archiv f. Hygiene*, xvi., 101) that the humidity and rise of temperature possess an appreciable influence on the animal organism.

Comparatively little attention has been paid to the quantity of nitrites present in the air of inhabited rooms, and directions for these compounds are not available for the general student. The object of the work here reported was to show that nitrites do exist in the air in appreciable though small quantity, that the amount of nitrites is varying under varying conditions, and that they increase in the same manner and under like circumstances as does carbon dioxide, thus indicating that they are products of combustion.

That nitrites do exist in the air of rooms is evident from the fact that 100 c.c. of pure water, treated with a mixture of 1 c.c. hydrochloric acid (1:4), 2 c.c. sulphuric acid, and 2 c.c. naphthylamine hydrochlorate solution, and

* *Technology Quarterly and Proceedings of Society of Arts*, ix., p. 238.

exposed to the air, rapidly takes on a deep pink colour, due to the absorption of nitrites from the air by the water, forming α -naphthylamine-azo-benzenesulphonic acid. For this reason the various "standards" used in estimating the amounts of nitrites in water are always freshly prepared on making an analysis to prevent as much as possible any liability of error in the determination.

The work described below was carried on in the Walker Building of the Massachusetts Institute of Technology. This structure has the reputation of being one of the best ventilated in the country, the air in the laboratories being completely changed once in seven minutes, so that some of the results obtained will be somewhat different from those possible in places where not so much attention is given to obtaining a good supply of fresh air.

The first experiment tried was to determine the rate of absorption of nitrites by water in various laboratories. 100 c.c. of re-distilled water were placed in each of three porcelain evaporating dishes (15 c.m. in diameter), which gave in each case a superficial area of water exposed to the air of about 95 sq. c.m. These were then allowed to stand for specified times in a room, and the amounts of nitrites absorbed by the water determined in the usual manner. The re-distilled water used was that employed by the Massachusetts State Board of Health in making its various standards for determining the amounts of ammonia, nitrites, and nitrates, thus insuring the freedom of the water from these substances.

The absorption of nitrites by water in Room 36, Walker Building, was first determined. During the day on which this experiment was carried on no water analyses were in progress. One gas burner had been in use a part of the morning. In the latter part of the afternoon two lamps were burning till after five o'clock. An apparatus for furnishing hot water, heated by means of gas, was put into service at 3.30 p.m., and left burning till after five o'clock. In this room there were also, on an average, three persons employed during the day.

The three porcelain dishes containing each 100 c.c. of best re-distilled water, free from nitrites, were placed side by side on a desk and exposed to the air for varying lengths of time, being then treated with the reagents named above, the depth of colour produced by this means being compared to that of standard potassium nitrite solutions (1 c.c. containing 0.0000001 grm. nitrogen as nitrite) treated with the same reagents.

An analogous experiment was tried in Room 38 of the same building. During the morning one lamp had been burning one hour. Work was carried on by three persons during various portions of the day, they, however, not requiring the use of any gas burners. The three porcelain dishes were placed in position on a desk at two o'clock in the same manner as in the preceding case.

The third trial of the series was made with the air in Room 39. Four Bunsen burners had been in use all day, being turned out at five o'clock. Three students had been at work the greater part of the time, and at occasional intervals others were also present. The first two samples of water were placed in position at 2 p.m., and the third, which was exposed for seventeen hours, was placed in position at 4 p.m. The results of these series of experiments are given in the following table:—

Room.	Hours of Exposure.			
	1.	2.	17.	19.
	C.c. equivalent nitrite solution.			
36	2.5	3.5	—	57.2
38	3.5	8.5	—	72.7
39	8.0	13.5	84.2	—

On examining the above results we notice the following:—

1. Even in the air of the best ventilated rooms where gas is burned nitrites exist.
2. Water exposed undisturbed to the air absorbs nitrites there existing.

3. The amount of nitrites so absorbed increases in almost direct proportion to the time the water is exposed, being also dependent, however, on the nature of the work carried on in the room.

4. On burning illuminating gas some of the nitrogenous constituents, though small in amount, are incompletely oxidised to nitrites.

(To be continued).

ON THE INVERSION OF SUGAR BY SALTS.*

No. II.

By J. H. LONG.

(Continued from p. 216).

Ammonium Ferrous Sulphate.

BUT one experiment was made with this salt, a very nice crystallised preparation was used.

Experiment 8.

$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. N/2.

In 500 c.c., 100 grms. of sugar + 49 grms. of sulphate.

A = 17.08.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
0	12.93°	—	—	—
17	12.49	0.44°	0.01134	0.00066
45	11.74	1.19	0.03137	0.00069
75	10.93	2.00	0.05409	0.00072
105	10.13	2.80	0.07776	0.00074
165	8.60	4.33	0.12698	0.00077
225	7.30	5.63	0.17368	0.00077
345	4.60	8.33	0.29048	0.00084
465	2.85	10.08	0.38739	0.00083
525	2.20	10.73	0.42972	0.00082
				0.00076

The coefficient is seen to be low, but nearly a constant. In this case, as in that of the ferrous sulphate, the mixture became slightly turbid on heating.

Zinc Sulphate.

It is practically difficult to secure a good preparation of zinc sulphate crystallised without the addition of a trace of sulphuric acid. In absence of the acid crystallisation is very slow. The preparation used below was made from a chemically pure commercial sample, by crystallising with a trace of acid first and then from pure water, after heating the solution with pure zinc. The final crystallisation, to secure 50 grms., required weeks for its completion. In my former paper attention was called to the fact that inversion with zinc sulphate is very slow, which is well shown below. The experiment was closed when the sugar was about half inverted, and as the coefficient is not regular, it is not possible to estimate accurately the mean rate for the whole period.

Experiment 9.

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. N/2.

In 250 c.c., 50 grms. of sugar + 17.94 grms. of the sulphate.

A = 17.25.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
0	13.10	—	—	—
15	12.88	0.22°	0.00558	0.00037
45	12.35	0.75	0.01935	0.00043
105	11.34	1.76	0.04674	0.00044
165	10.40	2.70	0.07393	0.00045
285	8.48	4.62	0.13539	0.00048
405	6.51	6.59	0.20903	0.00052
525	4.68	8.42	0.29083	0.00055

* From the *Journal of the American Chemical Society*, xviii., No. 8, August, 1896.

Manganous Sulphate.

After several attempts a salt was obtained crystallised from perfectly neutral solution. Some of the crystals were so irregular in outline that it was not possible to determine from inspection whether they contained 4 or 5 molecules of water. Determination of SO_4 in the product showed, however, that a very small amount only of the latter salt was present. In making the solutions I assumed for convenience that the compound had the formula $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, and weighed out accordingly.

As I pointed out in my former paper, a solution of manganous sulphate and sugar undergoes a peculiar decomposition when heated, in which a very fine dark substance is thrown out from solution. The amount of this is so small that I could not collect enough for tests in the work done; but it is still sufficient to make the polarimeter readings very difficult. All solutions had to be filtered before examination, but even with this precaution the readings were often obscure.

Experiment 10. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. N/2.

In 250 c.c., 50 grms. of sugar + 13.94 grms. of sulphate.

 $A = 34.80$.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
0	26.50°	—	—	—
45	26.33	0.17°	0.00213	0.000047
75	26.15	0.35	0.00439	0.000058
135	25.76	0.74	0.00934	0.000069
195	25.05	1.45	0.01848	0.000095
315	22.33	4.17	0.05543	0.000176
435	19.84	6.66	0.09226	0.000212
555	16.75	9.75	0.14277	0.000257

Experiment 11. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. N.

In 250 c.c., 50 grms. of sugar + 27.88 grms. of sulphate.

 $A = 34.75$.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
0	26.45°	—	—	—
15	26.25	0.20°	0.00250	0.00017
45	26.00	0.45	0.00566	0.00013
75	25.75	0.70	0.00883	0.00012
135	24.90	1.55	0.01981	0.00015
195	23.00	3.45	0.04541	0.00023
315	18.20	8.25	0.11770	0.00037
435	14.45	12.00	0.18397	0.00042
555	9.50	16.95	0.29053	0.00052

Experiment 12. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. 2N.

In 250 c.c., 50 grms. of sugar + 55.76 grms. of sulphate.

 $A = 34.42$.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
0	26.12°	—	—	—
30	25.12	1.00°	0.01280	0.00043
90	22.80	3.32	0.04405	0.00049
150	17.82	8.30	0.11984	0.00080
220	12.33	13.79	0.22231	0.00101
338	4.60	21.52	0.42622	0.00126
450	0.27	25.85	0.60383	0.00134
570	-3.80	29.92	0.88360	0.00155

Experiment 13. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. 3N.

In 250 c.c., 50 grms. of sugar + 83.64 grms. of sulphate.

 $A = 34.00$.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
0	25.70°	—	—	—
30	24.22	1.48°	0.01933	0.00064
90	18.76	6.94	0.09915	0.00110
150	11.50	14.20	0.23481	0.00156
220	4.75	20.95	0.41587	0.00189
338	-2.69	28.39	0.78252	0.00232
450	-6.25	31.96	1.22185	0.00272
570	-8.05	33.75	2.13354	0.00363

The rates of inversion cannot be directly compared in the above experiments because the latter were not carried

to completion. In the first case over one-third of the sugar originally present was inverted; in the second case almost exactly one-half; in the third case about six-sevenths; while in the last case the inversion was very nearly complete. By plotting the results it is possible to determine approximately the rate of inversion when just one-half of the sugar has been inverted, and this I have done. The results are given below, and show that the coefficients, K, are nearly proportional to the concentrations, these being referred to that of the half-normal solution as unity.

Conc.	K.
1	(0.00032)
2	0.00054
4	0.00109
6	0.00172

The first coefficient (0.00032) is uncertain because it was found by a rather wide extrapolation, but between the others there is fair agreement.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Special General Meeting, October 30th, 1896.

Captain ABNEY, President, in the Chair.

THE Secretary having read a summary of the replies sent by Members to a circular which had been addressed to them during the last Session, a series of Resolutions drawn up by the Council bearing on the points raised by this circular were adopted. The chief of these Resolutions were to the following effect:—(1) That the subscription to the Society be raised to £2 zs. (2) That present Life Members be invited to voluntarily subscribe £1 is. annually to the funds of the Society, or to compound for this annual contribution. (3) That a guarantee fund be instituted. (4) That in future Members of the Society be styled Fellows of the Physical Society of London.

In the course of the discussion on these Resolutions the President, Secretary, and Treasurer gave an account of the financial position of the Society, and explained that at present each Member receives from the Society, in the shape of Proceedings and Abstracts, printed matter which costs the Society more than the amount of the annual subscription.

The Ordinary Science Meeting was then held.

A letter was read from Lord Kelvin thanking the Society for the Address which the President, on their behalf, had recently presented to him.

Prof. W. STROUD read a paper, by himself and Mr. J. B. HENDERSON, on a "Satisfactory Method of Measuring Electrolytic Conductivity by means of Continuous Currents."

The method consists in placing a balancing electrolytic cell in the arm of the Wheatstone's bridge adjacent to the arm containing the chief electrolytic cell, so that the electromotive force of polarisation in the two cells neutralise each other's effect on the galvanometer. The authors find that if the resistance of the arms of the bridge are high (20,000 ohms), and if an E.M.F. of about 30 volts is used in the battery circuit, then the resistance of a solution (of potassium chlorate in their experiments) can be determined to within about one part in two thousand. With a D'Arsonval galvanometer the balancing cell is so efficacious that it is impossible to tell that it is not a metallic resistance that is being measured.

Prof. PERRY asked if the authors had tested whether the difference in resistance of the two cells was pro-

portional to the difference in length of the liquid columns.

Mr. APPELYARD said he had found that the resistance of an electrolyte appeared to vary, because in the ordinary arrangement the cell was short circuited through the arms of the bridge. He suggested as a remedy the making and breaking of the circuit by a special key, so arranged that except when taking a reading the cell is on open circuit.

Mr. BLAKESLEY asked if the authors had tried the method in which the resistances are adjusted till, when the battery circuit is broken, there is no immediate change in the galvanometer deflection. It is possible by this method to measure a resistance of between 6,000 and 10,000 ohms to within 0.1 per cent.

Prof. AYRTON said the method referred to by Mr. Blakesley was the ordinary "false zero" method. In using this method you were working to a continuously altering zero; in Prof. Stroud's method, however, the zero was constant.

Mr. APPELYARD said he had found the "false zero" method troublesome to use.

Prof. STROUD, in reply, said they had not tested the proportionality between the resistance and length, and they had not tried the "false zero" method.

Mr. APPELYARD then exhibited a number of different forms of Electrical Trevelyan Rockers.

The most interesting one consisted of two rods of carbon fixed to a wooden sounding-board, with a third carbon rod lying across the other two so as to form a microphone. A fairly strong current is passed through this microphone, and through two electro-magnets which act on the prongs of a tuning-fork fixed to the sounding-board. The tuning-fork acts on the microphone, which, by making and breaking the current, keeps the fork in vibration.

A cylinder of carbon, forming the "knife-edge" of a small pendulum supported on two horizontal carbon rods, kept the pendulum in violent oscillation as long as a current passed from one of the horizontal rods, through the movable cylinder and out through the other horizontal rod.

The Society then adjourned till November 13th.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 16, October 19, 1896.

New Researches on the Decomposition of Sugars under the Influence of Acids, and especially on the Production of Carbonic Acid.—MM. Berthelot and G. André.—This paper will be given at some extent as early as possible.

Comparative Digestibility of Cocoa-nut Butter and Cows' Butter.—In a course of experiments it appeared that the digestibility of vegetable butter (that obtained from the cocoa-nut) is 98 per cent, whilst that of cows' butter (i.e., that obtained from the milk of the cow) is 95.8 per cent.

Certain Coloured Reactions of Brucine; Researches on Nitrous Nitrogen in presence of Sulphites.—Will be inserted in full.

Certain Peculiarities of the Curves of Solubility.—H. Le Chatelier.—A purely mathematical paper.

Property of Discharging Electrified Conductors produced in Gases by the X Rays and by Electric Sparks.—E. Villari.—Gases traversed by the X rays acquire the

property of discharging electrified conductors. It results from my most recent researches that they acquire this property rapidly and retain it for some time. In fact, on exciting by the X rays a gas contained in a zinc receiver with a slender wall of aluminium, and propelling it rapidly by a long, thick glass tube (3×1000 c.m.) against an electroscope, the latter is seen to be discharged. On the contrary, it is not discharged if the current of gas is not excited by the X rays. The property of discharging conductors is lost by degrees according as the gas passes through longer or shorter tubes, which may be of glass or metal, insulated or not. These experiments have been made with air, oxygen, coal-gas, hydrogen, and a mixture of air and vapours of ether and of carbon disulphide. These gases acquire the same property on passing through a glass tube traversed by a series of induction sparks strengthened by a condenser. The length of the sparks beyond 4 to 5 m.m. has no perceptible influence on this phenomenon. But the efficacy for the discharge is nearly doubled if four sparks are produced in the tube instead of a single one. The induction sparks if not reinforced have an action distinctly weaker, which increases up to a certain limit with the length of the spark and diminishes then down to zero. The efficacy of the reinforced sparks does not decrease if another is produced outside of the tube, but it diminishes distinctly if we augment the resistance of the induced circuit by means of a column of solution of copper sulphate. The efficiency for the discharge increases a little with the rapidity of the gaseous current and decreases with the length of the tube which conducts the gas to the electroscope. This property cannot be ascribed to a heating produced in the gas by the sparks; on the one hand they heat it only slightly, and on the other hand, if the gaseous column is strongly heated by means of a flame, but not activated by sparks, does not discharge the electroscope.

Succession of the Atomic Weights of Simple Bodies.—M. Delaunay.—This paper will be inserted in full.

Phosphopalladic Ethers, Ammoniacal Derivatives of the Phosphopalladous and Phosphopalladic Ethers.—M. Finck.—An account of phosphopalladic ethyl ether, the corresponding methyl ether, the ammoniacal derivatives of the ethyl and methyl-phosphopalladous ethers, the corresponding palladic ethers, and the action of the compound ammonias upon the ethyl and methyl phosphopalladous ethers, and also that of pyridine upon the same ethers.

The Action of the Electric Effluve on the Property of Gases to discharge Electrified Bodies.—Emilio Villari.—It results from my former paper that gases acquire the property of discharging electrified bodies not only by the action of the X rays, but also if they are traversed by a series of energetic electric sparks. Further researches enable me to affirm that gases traversed by the sparks seem to acquire a greater conductivity of heat. Two glass tubes, short and thick, connected by other slender tubes, were traversed by one and the same gaseous current. In the first it was possible to produce with platinum wires four sparks furnished by an inductor and reinforced by a condenser; in the second tube there was a small platinum spiral. Through the tubes we drive a gaseous current, and we can, by means of a battery, raise the small spiral to nascent redness; we then activate the tube with sparks; the small spiral cooled and became dark. The experiments were executed with air and coal-gas. The property acquired by gases of discharging electrified bodies might perhaps be ascribed to a kind of dissociation of the gaseous molecules. Guided by this supposition I wished to try the effect of the electric effluve upon gases. By means of an ozoniser I drove upon the electroscope a current of oxygen and of air. I saw that the electroscope was not discharged. It was the same with a current of hydrogen or of coal-gas. The effluve, therefore, does not produce in these gases the power of discharging con-

ductors. But what is particularly remarkable, the effluve seems to destroy in gases the power which they have previously acquired. A gaseous current activated by X rays or by sparks was driven against an electroscope after having passed through a glass ozoniser. With an inactive ozoniser the electroscope was at once discharged, whilst it was no longer discharged on activating the ozoniser. These experiments were performed with air, oxygen, and coal-gas. It is known that the combustion products of flames rapidly discharge conductors. In a recent paper I have shown that this property diminishes a little if the products are cooled by a refrigerating current of water of about 2 metres in length; if we pass these products, hot or cold, through an ozoniser in activity they lose completely their efficacy for discharging conductors.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held Monday afternoon (the 2nd inst.), Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—Mr. George Cawston, Mr. J. Broughton Dugdale, J.P., D.L., Mr. Henry Harben, J.P., and Mr. John H. Usmar. The special thanks of the Members were returned to the Proprietors of the *Times*, Dr. Ludwig Mond, F.R.S., Prof. Dewar, and Sir Andrew Noble, for their donations to the fund for the promotion of Experimental Research at Low Temperatures. It was also announced that the Christmas Lectures specially adapted for children will this year be given by Prof. Silvanus P. Thompson, F.R.S., his subject being "Visible and Invisible Light"; and it was reported that the Managers had elected Prof. Augustus D. Waller, M.D., F.R.S., Fullerian Professor of Physiology for three years, the appointment to date from January 13th, 1897, and also that the managers had appointed Dr. Alexander Scott, M.A., D.Sc., to be Superintendent of the Davy Faraday Research Laboratory of the Royal Institution, the Directors already appointed by the Managers being Lord Rayleigh and Professor Dewar. After the Meeting the Members inspected the new rooms which have been lately added to the Library of the Royal Institution, through the munificence of Dr. Ludwig Mond, F.R.S., which rooms will provide increased accommodation for the Members on the occasion of the Friday Evening Meetings.

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1929.

ACTION OF METALS AND THEIR SALTS ON THE ORDINARY AND ON THE RÖNTGEN RAYS—A CONTRAST.*

By J. H. GLADSTONE, F.R.S., and W. HIBBERT.

THIS paper, which was communicated to Section B of the British Association at Liverpool last September, was a preliminary notice of an investigation that is still on hand. It is an extension in a new direction of previous work on the optical properties of metals and salts, the results of which have been published from time to time during the last thirty-nine years. The present experiments were made in Mr. Hibbert's laboratory in the Polytechnic, Regent Street, London, the method adopted being very similar to that generally employed for X ray work. The paper was accompanied by numerous photographs, most of which included a scale made of different thicknesses of aluminium.

I. Action of Metals on the Ordinary Rays.

It is well known that metals in the solid condition absorb ordinary light completely, though very thin plates of silver and gold transmit certain rays to a small extent. It is, however, a remarkable fact that when these metals combine with an acid radical, they cease to absorb ordinary light. This is quite true in regard to the metals of the alkalis, of the alkaline earths, and of the earths, as well as in regard to most of the ordinary metals. There are two groups of metals of which the remark cannot strictly be made, for they exhibit the absorption of certain rays, while others are transmitted. These are the great iron group, and the group that includes gold and most of the noble metals; all of these are to be found in the eighth column of Mendeleeff's table, or near it. There is, we believe, no soluble metallic salt known which is absolutely opaque.

The solutions of the colourless salts are themselves colourless when the solvent is colourless. The solutions of the coloured salts are generally, but not always, of the same colour as the undissolved salt.

II. Action of Metals on the Röntgen Rays.

The action on these rays exhibits a great contrast. All the metals, as far as they have been examined, instead of wholly absorbing, transmit the Röntgen rays more or less. This was one of the earliest observations of Röntgen, and it has been confirmed by many other observers. We have extended the list to the alkaline metals, and find that lithium (the metal of lowest density) is almost absolutely transparent; and there is every gradation between it and the noble metals, which are practically opaque, the slightly transparent gold being amongst the most opaque for X rays.

When the metals combine with acid radicals, they exhibit the same, or nearly the same, absorption as they do when in the uncombined condition. Thus, in a score of instances, we have found that the formates and acetates of lithium, potassium, sodium, calcium, zinc, aluminium, and lead, showed an absorption analogous to that of the metals themselves, and we have met with no marked exception. This is absolutely different from what occurs in the case of the ordinary rays.

In the few instances we have yet tried, the solution of a salt in water has the same action on the Röntgen rays

as the salt itself. The best instance is that of formate of potassium, which dissolves in so little water that the effect of the solvent is negligible.

III.—The Order of Absorption.

The order of absorption of the X rays by metals was at first supposed to be the same as that of their density. We find, however, with the alkali metals, that the order of absorption is lithium, sodium, potassium, while that of their density is lithium, potassium, sodium.

It has been shown by Prof. Barrett (*Proceedings Royal Dublin Society*, May, 1896) and others that the absorption follows the order of the atomic weights rather than that of the density.

From certain experiments which we have recently made on the refraction of metals, we were especially interested in observing whether the order was that of the atomic weights, or that of the equivalents. It was tested in the case of potassium and calcium, which have practically the same atomic weights—39 and 40—though their equivalents differ, being 39 and 20. It was found that whether tested by the uncombined metals or by their salts, the absorptions of the Röntgen rays by the two metals are about the same for thicknesses answering to the atomic weights, while they are very different for thicknesses answering to the combining proportions. The three metals, sodium, magnesium, and aluminium (atomic weights 23, 24, 27; combining weights 23, 12, 9, respectively) showed the same thing, though not so clearly. Mercury was found to give practically the same amount of absorption in the mercurous and mercuric acetates.

In dealing with metals, whether uncombined or in salts, the order of their absorption for these rays is, in fact, that of their atomic weight, but the amount of absorption increases much more rapidly than the atomic weights themselves.*

In attempting to estimate the absorbent value of the different metals from their salts, we were led to prefer the formates, as the acid radical (CHO_2) has a low equivalent and has scarcely any absorbent effect. Where the formate was not available we adopted the acetate. Similarly, as lithium has next to no absorbent action on the Röntgen rays, its salts afford the best means of determining the effect of the different acid radicals.

The general law to which our experiments tend is, that the absorption of a dry salt, whether crystallised or not, is an additive property, the sum of the absorptions of its two constituents. The absorption of a solution is apparently that of the salt itself, plus that of the solvent.

ON METHODS OF DETERMINING THE DRYNESS OF SATURATED STEAM, AND THE CONDITION OF STEAM GAS,†

By Prof. OSBORNE REYNOLDS, M.A., LL.D., F.R.S.

(ABSTRACT).

IN certain recent attempts to ascertain the proportion of steam and water in the fluid which enters a steam-engine, by means of what is called the wire-drawing calorimeter, the published results show that there remains from 0 to 5 per cent by weight of water in the steam, after it has been drained by gravitation, in the same manner as the steam on which Regnault's experiments were made. This has necessarily excited great interest and is naturally welcome, as it apparently brings the per-

* The order of progression in the absorption of different salts has been to a certain extent worked out previously by Novák and Sulc, *Zeit. Ph. Ch.*, February, 1896; and by Blennard and Labesse, *Comptes Rendus*, March, 1896. See also remarks made by Prof. Dewar at the Royal Society, as reported in the *Times* of February 15.

† Read before the Manchester Literary and Philosophical Society, November 3, 1896.

* Read before the British Association (Section B), Liverpool Meeting, 1896.

formance of the engines by so much nearer perfection. Although the results of these recent experiments appear to show the condition of dry saturated steam to be other than that on which Regnault's experiments were made, and from which the present steam tables have been calculated, still these tables have been used in deducing the percentage of water latent in the steam. Whereas, if the latent water exists, it must have existed in the steam used by Regnault, and the steam tables must also be subject to identical corrections; and, consequently, the percentage of theoretical performance of steam engines would be unchanged.

It is then pointed out that, in the reduction of such of these results as have been published, use has been made of Regnault's determination of the specific heat at constant pressure of steam gas (0.48) in a manner which is not consistent with the theory of thermodynamics. Thus, in Rankine's notation, S_1 is the weight of steam per lb. of fluid, and H_1 the total heat per lb. from 0°C. to T_1° , h_1 the heat required to raise water per lb., and H_2, h_2, T_2 , the corresponding values for saturated steam at the pressure after wire-drawing, and T_3° the observed temperature after wire-drawing.

The notation assumed for the equation of heat, neglecting incidental losses, is—

$$S_1(H_1 - h_1) + h_1 = H_2 + 0.48(T_3^\circ - T_2^\circ) \dots \text{r.}$$

Whereas, it has been proved by Rankine that the thermodynamic expression for the total heat in superheated steam at $T_3^\circ \text{C.}$, provided it has reached the condition of steam gas, to which the 0.48 only applies, is—

$$C_1 + 0.48(T_3^\circ - T_0^\circ).$$

C_1 , being a constant, depends only on the temperature of the water (T_0°) from which the steam is produced, the value of which from 0°C. is 606.7, approximately, as deduced by Rankine.

Using Regnault's formula for H_2 , the right member of equation (1) becomes—

$$606.5 + 0.305 T_2^\circ + 0.48(T_3^\circ - T_2^\circ),$$

while the value by the thermodynamic formula is—

$$606.7 + 0.48 T_3^\circ,$$

which gives as the excess of heat over that assumed—

$$0.2 + 0.175 T_2^\circ.$$

This excess, if T_2 were 100°C. is 17.7 thermal units, and if the initial steam pressure were 200 lbs. above the atmosphere, the latent heat being 467.5 thermal units, the percentage of water it would evaporate at boiling-point is—

$$\frac{17.7}{467.5} = 3.8\%,$$

which is about as much as needs to be accounted for.

It is also shown that, in order to render Rankine's formula applicable to wire-drawing experiments, it is necessary that the wire-drawing should be continued till the steam is gaseous, whence arises the difficulty of securing that this state has been reached. This, however, may be secured by lowering the pressure gradually after wire-drawing, and so increasing the extent of wire-drawing while observing the temperature (T_3°), which, after falling, will gradually become constant as the wire-drawing increases, and, when constant, will be a definite indication of this gaseous state.

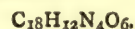
The necessary conditions to ensuring accuracy are then considered, and, in conclusion, it is stated that a research to verify these conclusions has been commenced by Mr. J. H. Grindley, B.Sc., in the Engineering Laboratory of Owens College, Manchester.

The Iodine Number of Cocoa Butter.—Dr. F. Filsinger.—The author has made comparative experiments on kaka beans, kaka-mass, and kaka chocolate. The highest iodine number found was 37.5 in a sample from Sumana, and the lowest, 33.5, was yielded by that from Machala-Guayaquil.

A NEW BLUE DYE OBTAINED FROM QUINONE.

By Dr. JAMES LEICESTER, F.C.S.,
Lecturer on Chemistry and Metallurgy at the Merchant Venturers' Technical College, Bristol.

WHEN benzoquinone, $\text{C}_6\text{H}_4\text{O}_2$, is heated in glacial acetic acid solution with O nitroaniline, $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{NH}_2$, a substance called dinitrodianilidoquinone is formed, having the following composition:—



0.1360 grm. of the substance yielded 0.2860 grm. of carbon dioxide and 0.0380 grm. of water.

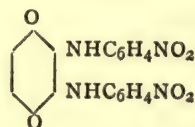
0.1420 grm. of the substance yielded 18 c.m. of nitrogen at 21°C. and under a pressure of 741 m.m.

Taking $\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_6$ as the formula—

Found by analysis.

C	56.84	57.35
H	3.15	3.10
N	14.73	14.84

These results would give the following graphic formula:—

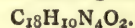


It can be easily crystallised from absolute alcohol. When pure it melts at 305°C.

If the dinitrodianilidoquinone, $\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_6$, be reduced by means of alcoholic ammonium sulphide, a dark green coloured powder is obtained which dissolves in acetic acid with an intense blue colour; the solution readily dyeing silk and woollen goods. The colour is a fast one, not fading with the action of sunlight, or coming out on washing. If dilute sulphuric acid be added in small quantities to the acetic acid solution a very strong fluorescence is obtained.

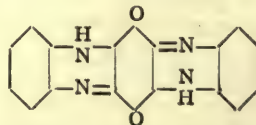
Light passing through the solution has a rich blue colour; the light reflected from the solution being a deep red in colour.

An analysis of the substance gives the following results.



	Theory.	Found.
C	68.7	68.5
H	2.3	3.9
O	—	—
N	17.8	17.7

The following formula represents its probable constitution:—



A cheaper process is necessary for the manufacture of the dye, which is known commercially as Istarine.

City and Guilds of London Institute.—The following is a list of Scholarships awarded in connection with the present Session, 1896-97, of this College:—Clothworkers' Scholarship (£60 a year, with free education for two years), L. P. Wilson; Mitchell Scholarship (£40 a year, with free education for two years), R. S. Potter; Clothworkers' Technical Scholarship (£30 a year, with free education for two years), E. W. Cook; David Salomons Scholarship (£50), E. W. Marchant; John Samuel Scholarship (£30), H. W. Hanbury; Institute's Scholarships (free education for three years), F. S. Miller, J. I. Hunter, F. W. Fawdry.

ON THE INVERSION OF SUGAR BY SALTS.*

No. II.

By J. H. LONG.

(Continued from p. 232).

Manganous Chloride.

THE salt used was purified by several crystallisations from the best obtainable Schuchardt product.

Experiment 14.

$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. N/4.

In 250 c.c., 50 grms. of sugar + 6.18 grms. of chloride.
 $A = 35.00$.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
0	26.70°	—	—	—
15	26.60	0.10°	0.00124	0.00009
45	26.30	0.40	0.00499	0.00011
75	26.00	0.70	0.00878	0.00012
135	25.25	1.45	0.01838	0.00014
255	22.66	4.04	0.05327	0.00021
375	18.75	7.95	0.11190	0.00030

The high initial rotation here is very extraordinary, corresponding to a specific rotation of 66.75°.

Experiment 15.

$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. N/2.

In 250 c.c., 50 grms. of sugar + 12.35 grms. of chloride.
 $A = 34.84$.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
0	26.54°	—	—	—
15	26.45	0.09°	0.00113	0.00008
45	26.16	0.38	0.00476	0.00011
75	25.85	0.69	0.00869	0.00012
135	24.52	2.02	0.02594	0.00019
255	22.26	4.28	0.05693	0.00022
375	17.15	9.39	0.13639	0.00036
495	13.00	13.54	0.21370	0.00043
555	11.52	15.02	0.24498	0.00044

Experiment 16.

$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. N.

In 250 c.c., 50 grms. of sugar + 24.70 grms. of chloride.
 $A = 34.63$.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
0	26.33°	—	—	—
15	26.12	0.21°	0.00264	0.00018
30	25.86	0.47	0.00593	0.00020
60	25.15	1.18	0.01505	0.00055
120	23.05	3.28	0.04321	0.00036
180	20.07	6.26	0.08659	0.00048
300	15.60	10.73	0.16105	0.00054

Experiment 17.

$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. 2N.

In 250 c.c., 50 grms. of sugar + 49.40 grms. of chloride.
 $A = 34.18$.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
0	25.88°	—	—	—
15	25.38	0.50°	0.00640	0.00043
45	23.91	1.97	0.02578	0.00057
75	22.21	3.67	0.04933	0.00065
135	18.25	7.63	0.10971	0.00081
195	14.80	11.08	0.17016	0.00087
345	5.25	20.63	0.40183	0.00116

No very plain relation can be found connecting these rates of inversion. The coefficients corresponding to the time of completion of one-third of the inversion are here given.

Conc.	K.
1	(0.00038)
2	0.00041
4	0.00055
8	0.00088

The first coefficient had to be estimated and is uncertain.

Ferrous Chloride.

Considerable difficulty was experienced in preparing a solution of ferrous chloride devoid of traces of free acid. A weighed excess of pure iron wire was covered with water in a small flask, and then the calculated volume of titrated hydrochloric acid was added in amount just sufficient to produce the solution of required strength. The mixture was gently warmed and allowed to stand a short time. Warming was repeated at intervals through several hours, until the liberation of hydrogen became very feeble. The solution so obtained stood five days in the presence of the excess of iron, being boiled twice in the interval, and was then filtered cold into the sugar solution, which was made up to the proper volume with fresh distilled water.

The actual strength of solutions made in this manner was determined by titration later. The two following were almost exactly normal and half-normal.

Both solutions became turbid on heating and had to be filtered before polarisation for the first tests. After the lapse of about two hours the cloudiness disappeared, and the solutions then taken from the thermostat were clear enough for direct polarisation.

Experiment 18.

FeCl_2 . N/2.

In 250 c.c., 50 grms. of sugar + 7.925 grms. of chloride.
 $A = 16.18$.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
0	12.03°	—	—	—
15	9.47	2.56°	0.07507	0.00500
45	7.44	4.59	0.14517	0.00322
105	5.00	7.03	0.24783	0.00236
165	3.83	8.20	0.30725	0.00186
285	1.90	10.13	0.42749	0.00150
405	-0.50	12.53	0.64696	0.00160
525	-2.01	14.04	0.87884	0.00167

Experiment 19.

FeCl_2 . N.

In 250 c.c., 50 grms. of sugar + 15.85 grms. of chloride.
 $A = 15.71$.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
0	11.56°	—	—	—
15	9.40	2.16°	0.06424	0.00428
45	6.88	4.68	0.15360	0.00341
105	4.75	6.81	0.24679	0.00235
165	3.56	8.00	0.30913	0.00188
285	1.15	10.41	0.47190	0.00165
405	-1.42	12.98	0.76002	0.00187
525	-3.25	14.81	1.24194	0.00236

These results are very surprising, inasmuch as they show but little difference between the rates for the two concentrations. In both instances the rates rapidly decrease from the beginning, and after the sugar has been about half inverted they increase a little. I give next some results from solutions which had not been boiled so thoroughly, and which may have held a little free acid.

Experiment 20.

FeCl_2 . 0.52 N.

In 250 c.c., 50 grms. of sugar + 8.242 grms. of chloride.
 $A = 34.00$.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
0	25.70°	—	—	—
15	20.00	5.70°	0.07969	0.00531
45	12.80	12.90	0.20720	0.00460
75	9.00	16.70	0.29343	0.00391
105	6.19	19.51	0.37041	0.00353
165	2.42	23.28	0.50129	0.00304
285	-1.95	27.65	0.72771	0.00256
345	-3.96	29.66	0.89399	0.00258
405	-5.30	31.00	0.95436	0.00260

* From the *Journal of the American Chemical Society*, xviii., No. 8, August, 1896.

Experiment 21.

FeCl₂. 0.98 N.
In 250 c.c., 50 grms. of sugar + 15.53 grms. of chloride.
A = 33.60.

t.	a.	z.	Log. $\frac{A}{A-z}$	$\frac{1}{t}$ log. $\frac{A}{A-z}$
0	25°30'	—	—	—
15	19°84'	5°46'	0.07702	0.00513
45	14°20'	11°10'	0.17416	0.00387
75	11°80'	13°50'	0.22314	0.00297
105	9°88'	15°42'	0.26675	0.00254
165	7°65'	17°65'	0.32358	0.00196
285	1°45'	23°85'	0.53734	0.00188
345	-1°50'	26°80'	0.69383	0.00201

The effect of free acid is not apparent. Six other experiments were made with normal and half-normal ferrous chloride solutions, the results of which were very similar to those above. In all cases the constant was found to increase before the completion of the inversion.

The constant for 0.009 N hydrochloric acid was determined for comparison at the same temperature, $t=85^\circ$, and with the same amount of sugar. It was found—

$$K=0.0051.$$

(To be continued).

THE NEW ELEMENTS OF CLEVEITE GAS.

By J. R. RYDBERG.

THE excellent investigations of Runge and Paschen on the spectrum of cleveite gas (*Astrophysical Journal*, iii., 4—28, 1896) have made the existence of another new element besides helium very probable.* But the method of forming the spectral series seems to rest upon rather an insecure basis, although by the help of the relation between the principal series and the sharp series (second subordinate series of Kayser and Runge), which I long ago pointed out, it would have been very easy to state clearly the true connection. The relation in question, which comprehends the above-mentioned series in a single common formula, is derived from the observation that the first term of a principal series forms at the same time the first term of the corresponding sharp series, or, to state the same thing in another form,—

The difference between the common limit of the nebulous and the sharp series and the limit of the corresponding principal series gives the wave-number† of the common first term of the sharp and the principal series.

If we designate the limits of the series by D (nebulous), S (sharp), P (principal series), the order of the series by subscripts to the symbols of the elements (stronger series 1, weaker 2), and the mean of D and S by M, we have for the alkali metals:—

	D	S	M	P
Li	28582.92	28582.16	28582.54	43482.53
Na ₁	24468.89	24471.36	24470.13	41452.61
Na ₂	24486.08	24488.55	24487.32	41452.61
K ₁	21959.52	21951.39	21955.46	35008.92
K ₂	22017.37	22009.24	22013.31	35008.92
Rb ₁	20861.25	20877.05	20869.15	33706.66
Rb ₂	21098.83	—	21098.83	33705.59

Hence, if we call P₁ the first term of a principal series, we have—

* For the new elements I use the symbols A (Argon), He (Helium), Pa (Parhelium).

† By wave-number I mean the number of waves in 1 c.m. See Svenska Vetensk. Akad. Handl., xxiii., 35, 1890.

	P-M	P ₁	Diff.
Li	14899.99	14903.03	- 3.04
Na ₁	16982.48	16972.70	+ 9.78
Na ₂	16965.29	16955.51	+ 9.78
K ₁	13053.46	13041.72	+ 11.74
K	12995.61	12984.63	+ 10.98
Rb ₁	12837.51	12798.95	+ 38.56
Rb ₂	12606.76	12575.18	+ 31.58

For Pa and He, on calculating the limits by the same method which I have used for the other elements, I have found the following values:—

	D	S	M	P
Pa	27174.47	27175.00	27174.74	32032.53
He	29222.70	29222.63	29222.67	38452.89

where the connection of the series is still undecided. By using the above-mentioned relation in the calculation of the values of P₁, two combinations present themselves, viz.,—

	P	M	P-M	P obs.	Diff.	Mean error.
Pa 32032.53	27174.74	4857.79	4900.65	- 42.86	20	
He 38452.89	29222.67	9230.22	8950.14	+ 280.08	40	
and—						
Pa 38452.89	27174.74	11278.15	—	—	—	
He 32032.53	29222.67	2809.86	—	—	—	

Although the calculated values of P₁ differ very considerably from the observed values, there can be no doubt that the first combination, which is the one chosen by Runge and Paschen, is the only possible one, for the lines calculated from the second were not observed. We meet here with the not very common case in which the calculated values greatly surpass the observations in accuracy, the limits of error for the values of M and P amounting at most to one unit, while the mean errors of the two values of P₁, determined with the bolometer, are 20 and 40 respectively. The differences found certainly exceed the errors to be expected, but the analogy with the spectra of the alkali-metals speaks so decisively in favour of an exact agreement between the values of P₁ and P-M, that I do not hesitate to ascribe the differences to errors of observation.

In order to judge better of the possibility of such differences I have examined the observations of Runge and Paschen, first reducing to wave-lengths the extreme values of the angular determinations (Runge and Paschen, p. 27). Thus we find:—

Observed maximum.	Observed minimum.	Mean.	Calculated value.
21040	19500	20400	20580.0
11450	10540	11170	10831.0

whence it appears that the calculated values lie within the limits of the observations. A closer examination shows that the angular determinations group themselves about well-defined means, by no means symmetrically, but so that the greater values are much more numerous than the smaller ones, and at the same time more distant from the closely concentrated central groups. At the line 11170 we even find two distinct groups. The distribution of the values is shown in the following table.

Wave-length according to K. and P.	No. of values of central group.	Range in angular values of central group.	Mean wave-length of central group.	No. of greater values.	No. of smaller values.	Diff. from mean of greatest value.	Diff. from mean of smallest value.
20400	7	0'.10	20580	12	3	2'.63	1'.17
11170 ₁	7	0'.15	11350	5	1	2'.32	0'.23
11170 ₂	9	0'.18	11190	4	2	1'.87	0'.73
7280	7	0'.10	7330	7	3	2'.82	0'.48

The greater deviation of the larger values seems to indicate a broadening of the lines in the direction of the

shorter wave-lengths. But, however this may be, the arithmetical mean of the observations under these circumstances gives by no means the most probable value of the quantity in question. I have therefore calculated the mean angular values of the central groups, and with the aid of the table (*loc. cit.*, p. 25) deduced the mean wave-lengths. For the first line the value thus obtained coincides exactly with the number calculated above; this, however, must be regarded as partly accidental. The third line does not agree as well as before, but still falls within the limits of the errors of observation. As to the second line, the doubling of the central group agrees perfectly with an hypothesis which had suggested itself previously and quite independently to explain the considerable discrepancy between observation and calculation. According to Runge and Paschen the strong Na lines in the visible and ultra-violet spectrum come out with great intensity; it could therefore scarcely be doubted that the line 11392.5 in the infra-red would also appear. It was also to be expected that in the bolometric determinations this line would form with the adjacent 10831.0 a single thermal maximum, and retain only a feeble indication of its double origin; the two thermal maxima, if they are still to be discerned as separate lines, ought at all events to appear very close together on account of the superposition.

But this is just what we have found, for according to Runge and Paschen the general mean of the wave-length determinations gives the value 11170, which would come out as the mean of the two wave-lengths mentioned above, if the intensity of the Na line were 1.5 times as great as that of the He line. The two values which I have calculated from the central groups of the observations would indicate a sharp Na line and a broad He line. The determinations do not, however, allow any perfectly definite conclusions to be drawn. But I believe that the preceding considerations will suffice to prove the importance of making further measures of the two infra-red lines. The accuracy attained by Lewis in his bolometric measurements (*Lewis, Astrophysical Journal*, ii., 1-25, 1895) would be quite sufficient to decide the present question. At all events I do not doubt that the calculated values 4858 and 9230 will be found for the wave-numbers of the lines *in vacuo*.

In this connection I cannot refrain from mentioning that the two new elements of clèveite gas, as well as argon, seem to be subject to a regularity regarding their atomic weights, to which I called attention some years ago (*Svenska Vetensk. Acad. Handl.*, xi., No. 13, 1886). The rule in question may be expressed as follows:—

If the atomic weights of the elements, which form the first rows of the periodic system, be reduced to the nearest integral numbers, the elements of uneven valency will have the form $4n-1$, and the elements of even valency the form $4n$.

On account of the uncertainty of the determinations of atomic weights and their increasing differences from integral numbers, the rule could be traced with some certainty only for the first twenty-two elements (to Fe inclusive). It shows here three exceptions, viz., Be (9 instead of 8), N (14 instead of 15), and Sc (44 instead of 43), but it gives place for He (4) and A (20), as well as for an element with the atomic weight 3, which would possibly answer to Pa. Spaces remain for elements with the reduced atomic weights 36, 44, and 47. The series of numbers is shown in the table which follows.

Of the six places formerly vacant in the present division two are probably permanently taken up by the new elements He and A. According to analogy these elements should have an even valency, while Pa might possess an atomic weight 3 and an uneven valency. For further particulars, as well as for regularities which appear on advancing further in the series of elements, I will refer to the paper mentioned above. It seems not quite impossible that the present exceptions may yet submit to the rule, when we consider the imperfection of our know-

ledge of the metals of the so-called rare earths (Be and Sc) and keep in view the surprising discoveries of the impurities of nitrogen.

"	1	2	3	4	5	6	7
Element	Pa	Li	B	N	Fl	Na	Al
P	?	7.01	10.9	14.01	19.06	22.995	27.04
$4n-1$	3	7	11	(15)	19	23	27
Element	He	Be	C	O	A	Mg	Li
P	4.0	9.03	11.97	15.96	19.94	24.3	28.3
$4n$	4	(8)	12	16	20	24	28
"	8	9	10	11	12	13	14
Element	P	Cl	K	Sc	—	V	Mn
P	30.96	35.37	39.03	43.97	—	51.1	54.8
$4n-1$	31	35	39	(43)	47	51	55
Element	S	—	Ca	—	Ti	Cr	Fe
P	31.98	—	39.91	—	48.0	52.0	55.88
$4n$	32	36	40	44	48	52	56

It is hardly possible that the approximation of the atomic weights to integral numbers, the correspondence in the number of elements in the two series of different valencies, and in the simultaneous evenness and unevenness of the integral numbers and the valencies, can be a mere chance.

The vacant places which still exist between Sc and Ti, as well as between the corresponding terms of the following periods, seem only to add further support to the rule proposed, inasmuch as they afford very necessary space for the numerous metals of the rare earths.—*Astrophysical Journal*, iv., No. 2, August, 1806.

TETRA-NITRO-CELLULOSE: A NEW EXPLOSIVE.

By H. N. WARREN, Principal Liverpool Research Laboratory.

WHEN dinitro-cellulose, or ordinary soluble pyroxylin, is further acted upon by means of a mixture composed of equal parts by volume of nitric acid 1.5 density, and concentrated sulphuric acid, there is, as is well known, produced a true trinitro compound, differing entirely from either of the above compounds as regards its solubility, and at the same time possessing far enhanced explosive properties.

If the resulting compound thus formed is again treated with a still more energetic dehydrating agent, composed of equal parts by weight of commercial vitriol and phosphoric anhydride, a further nitrogenous compound is obtained, which, after the usual washing and drying, presents a much more brittle structure than any of the preceding derivatives, in some cases even admitting of pulverisation, and altogether a much more formidable compound, even exploding by mere percussion, its explosive violence as compared with the former bodies being more than double.

When the compound is digested in a strong solution of potassium chlorate, and carefully dried, it is rendered extremely brittle, and thus readily admits of being pulverised, forming a true percussion agent. As far as can at present be ascertained the new explosive represents a tetra-nitro compound; but owing to its formidable explosive properties, necessitating considerable care in handling the same, further investigations are considered necessary, in order to arrive at a correct formula. The compound, when submitted to destructive distillation, in contact with moist caustic potash, evolves hydrogen gas, together with large quantities of methylic alcohol.

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SOME COLOUR REACTIONS OF BRUCINE;
DETECTION OF NITROUS NITROGEN
IN PRESENCE OF SULPHITES.

By P. PICHARD.

In our studies on the oxidising action of plaster in contact with nitrogenous organic matters we have been led to search for the existence of nitrous nitrogen in presence of oxygenous compounds of sulphur, sulphites, and hyposulphites, as well as alkaline and alkaline earthy sulphides. The most sensitive procedures for the detection of nitrous nitrogen are those of Griess, Tromsdorff, and Piccini. We have found that the colouration of brucine by hydrochloric acid on contact with a nitrite yields a reaction similar in sensitiveness to these procedures, and greater in presence of sulphites and hyposulphites.

A drop of solution of a nitrite mixed upon a porcelain plate with a drop of pure hydrochloric acid gives, with a particle of brucine, in at most 5 minutes a colouration which passes from vermilion to light yellow. We may thus detect one part of nitrous nitrogen in 640,000 parts of water. Hydrochloric acid under the same conditions gives nothing with a nitrate.

Chlorine and the hypochlorites do not colour brucine, but they give instantly an intense vermilion in the solutions of certain salts of brucine, the nitrate, the hydrochlorate, acetate, and sulphate. The sulphuric solution of brucine is the most rapidly and strongly coloured, as this acid more than others favours the formation of a yellow nitrated alkali, cacotheline, the ultimate result of oxidation.

The presence of a sulphite much diminishes the sensitiveness of the procedures of Piccini, Tromsdorff, and Griess for the detection of nitrous nitrogen.

Piccini's method is inapplicable in this case; traces of ferrous sulphite give in a dilute solution of ferrous sulphate, to which a little acetic has been added, the brown colour which shows the presence of nitrous nitrogen.

Tromsdorff's Method.—The proportion of 1/600 of SO_2 in the liquid reduces the sensitiveness of the reaction from 1/1,000,000 to 1/30,000; for 1/1800 of SO_2 the sensitiveness is 1/57,500.

Method of Griess.—1/2040 of SO_2 reduces the sensitiveness from 1/100,000,000 to 1/65,200; the sensitiveness is become more than 1000 times less.

Method with Brucine and Hydrochloric Acid.—1/2000 of SO_2 reduces the sensitiveness from 1/640,000 to 1/329,000, or only one-half.

In consequence of the direct addition of gypsum to soils, and the use of superphosphates in manures, the alkaline and alkaline earthy sulphides, sulphites, and hyposulphites may be found in notable quantity in drain waters, or the lixivium of a soil or a compost. If we wish to search for nitrous nitrogen in such waters we must first prove the presence or the absence of sulphides and sulphites. The sulphides are detected by lead acetate, silver acetate, or sodium nitro-prusside. We have satisfied ourselves that they do not affect the colour reaction of brucine.

Among the reactions indicated for the detection of sulphurous acid we do not know any for the present case in presence of a nitrite more distinct and more sensitive than the odour of this acid when it escapes into the air.

The liberation of sulphurous acid by the action of a strong acid, cold or hot, being accompanied by an escape of hydrogen sulphide (if the liquid contains a sulphide), and the odour of hydrogen sulphide being able to mask that of SO_2 , it is necessary in this case to eliminate the greater part of the hydrogen sulphide. This is easily affected by agitating the liquid with lead sulphate in fine powder. We decant, filter the liquid, and then treat it in a test-tube with a few drops of sulphuric acid, at first in the cold and then at ebullition. Traces of SO_2 may be detected in this manner.

If there is no sulphurous acid, we search for and determine nitrous nitrogen by the procedures of Tromsdorff or Griess.

If we have recognised the presence of a sulphite after having tested the liquid by the two methods above given without positive result, we have recourse to the use of brucine and hydrochloric acid, which will permit us to recognise 1/329,000 of nitrogen in presence of 1/2060 of SO_2 , and consequently to affirm the existence of nitrous nitrogen when the other methods fail to detect it.

The method of operation is that which we have given for the detection and determination of nitric acid by the aid of brucine and sulphuric acid.

The drainage water or the liquid derived from the lixiviation of a soil or a compost must be clarified and decolourised by filtration over finely washed animal charcoal.

The lixiviation must be effected with the smallest possible quantity of water, at most ten parts of water to one part of material. The mixture is rapidly raised to ebullition in a flask, which is then stoppered and shaken from time to time until completely cold. The liquid is then filtered over animal charcoal. From the filtrate we take a drop and place it upon a porcelain plate, and mix with it a drop of pure hydrochloric acid quite free from chlorine and nitrous products, and of sp. gr. 1.21. We spread it with a platinum wire so as to cover a surface of the size of a half-franc. We let fall into the middle of the liquid a fragment of brucine of the size of a pin-head. We wait five minutes at most until the appearance of a tint varying from vermilion to light yellow. If no colour appears we cannot affirm the presence of nitrous nitrogen.

The determination of small quantities of nitrous nitrogen, founded on the comparison of tints or the disappearance of these tints on dilution, is very uncertain in presence of alkaline or alkaline-earthly sulphites or hyposulphites.

We may correct the results obtained and render them more exact by determining the proportion of SO_2 contained in a part of the liquid.—*Comptes Rendus*, cxxiii., 590.

THE PRESENCE OF NITRITES IN THE AIR.*

By GEORGE DEFREN, M.S.

(Concluded from p. 231).

The investigation next carried out was to make a quantitative estimation of the nitrites by volume, by a method similar to that usually made use of in determining the quantity of carbon dioxide in the air of buildings. Two large bottles, the capacities of which were known, were placed side by side, and the air to be analysed was drawn into them, using suction, one tube reaching nearly to the bottom of the bottle. They were then tightly closed with rubber stoppers, and taken to the room where they were to be tested. 100 c.c. best re-distilled water, free from nitrites, were then introduced, the bottles allowed to stand, with occasional shaking, for more than twelve hours—in some cases for as many as twenty-four hours—before analysis. The water was then tested for nitrites in the usual manner.

Two samples of air from Room 36 were taken at 3.30 p.m. Fifteen lamps had been in use for about two hours. Three persons were employed during the day in this laboratory.

Two samples of air were also taken from Room 38 at nine o'clock in the morning. During the night preceding the room had been unoccupied, and no lamps had been in use up to the time of taking the samples. The bottles with 100 c.c. water were allowed to stand until next morning, and then analysed for nitrites.

* *Technology Quarterly and Proceedings of Society of Arts*, ix., p. 23

Two samples of air from Room 39 were taken at the same time as the preceding under the same conditions.

During the afternoon (at 3.30) two other samples of air were taken from this room in order to see whether any variation had taken place in the amounts of nitrites present. The samples were collected as in the previous cases. Eight Bunsen burners had been in use since 9 a.m., and were still burning at the time the air was taken for analysis. Three persons were employed in this laboratory during the day.

The amounts of nitrites absorbed by the water were determined in the usual manner. To see whether all the nitrites had been absorbed from the air in these bottles a little nitrite-free water was introduced after the above test. This water gave only a very faint colouration when treated with Griess's reagent, proving that nearly all the nitrite had been removed.

The temperature of the air was 20° C. at the time the analyses were made, and the barometric pressure was 758 m.m.

The results obtained are as follows, the nitrogen equivalent being calculated as nitrous anhydride:—

Room.	Time of taking sample.	Capacity bottle. C.c.	C.c. of nitrite equivalent.	Parts N_2O_3 in 10,000 air.
38	9 a.m.	8980	8.5	0.0140
38	9 a.m.	8870	8.3	0.0138
36	3.30 p.m.	8980	19.5	0.0319
36	3.30 p.m.	8870	18.9	0.0315
39	9 a.m.	8870	24.6	0.0408
39	9 a.m.	8320	25.7	0.0456
39	3.30 p.m.	8870	43.2	0.0690
39	3.30 p.m.	8320	40.0	0.0707

On inspecting the above results we see that (1) in the air of rooms the amount of nitrites is, as a rule, very small, on a clear day as little as 0.014 part in 10,000 parts air having been found; (2) the burning of illuminating gas and the presence of people seem to cause an increase in the quantity of nitrites present in the air.

Reference has been made as to the possibility of persons being a factor in causing the increase in quantity of nitrites in the air. That nitrites are formed through human metabolism is evidenced by the fact that the water in which the hands are washed give, on the addition of Griess's reagent, a very strong test for nitrites.

Trial was made to ascertain whether during the breathing process of man nitrites are exhaled. To this end 100 c.c. of re-distilled water were placed in a large test-tube and exhaled air blown through this water from the lungs for five minutes. The water was then treated for nitrites in the usual manner. No pink-coloured solution was formed, thus showing that expired air on passing through pure water does not give an indication of nitrites. This circumstance does not, however, prove conclusively that nitrites are absent in air which has passed through the lungs. There is a great probability that air containing a small amount of nitrite in the presence of a comparatively great quantity of oxygen, on passing through water oxidises these nitrites to nitrates, or even decomposes them to nitrogen. That this is evidently so is seen from the fact that a stream of air drawn through pure water by means of suction also failed to give any indication of nitrites, though water left exposed, undisturbed in this same air, gave a very decided test.

It has also been mentioned that rain-water obtained during a thunder shower contained more nitrogen as nitrite and nitrate (*loc. cit.*, see above) than rain tested when there were no electrical charges in the atmosphere. It seemed, therefore, probable that the larger part of the nitrites and nitrates were washed from the air during a rain storm. This was proved to be the case, for two porcelain dishes, containing each 100 c.c. of water, absorbed nitrites equivalent to 10 and 11 "standards," respectively, just before a rain storm. Immediately after the rain ceased, one dish, exposed for one hour, gave an indication of 0.2 "standard," while another gave 0.4

"standard," showing that the air is very thoroughly washed during a heavy fall of rain.

It will be seen from the above that the results which I have obtained, though not numerous, deal yet with a subject hitherto little considered. Some of the determinations do not directly confirm what I had expected. Further experiment may lead to definite results; and although it is my intention to continue the investigation, I also hope that this fragmentary presentation may stimulate others to further work on the subject.

THE SCIENTIFIC AND TECHNICAL DEPARTMENT OF THE IMPERIAL INSTITUTE.

A LECTURE was delivered at the Imperial Institute on Monday evening by Professor Wyndham Dunstan, F.R.S., the recently appointed Director of the Scientific and Technical Department, on some of the work of the Department. Sir Joseph Lister, Bart., D.C., President of the Royal Society, was in the chair, and there was a large audience, including representatives of science, commerce, and of India and the Colonies.

Professor Dunstan explained that the department was now provided with large and well equipped laboratories, occupying the whole of the west corridor of the second floor of the Imperial Institute. The equipment of this was finished at the commencement of October, and there was at the present time a staff of skilled chemists at work investigating a variety of natural products, derived from India and the Colonies, chiefly with a view to their commercial utilisation. The necessary funds for the appointment of an adequate staff to commence operations have been provided by the Royal Commissioners of the 1851 Exhibition, whilst the Goldsmiths' Company furnished the complete equipment for the laboratories, and also provided much of the apparatus. The department has therefore been created and endowed without pecuniary help from the Imperial Government. The Salters' Company had rendered important assistance to the undertaking by endowing a Research Fellowship of the annual value of £150, it being understood that the Salters' Research Fellow shall primarily devote himself to the investigation of the chemistry of medicinal plants, especially those derived from India and the Colonies. The principal work which the Department is now prepared to undertake was summarised as follows:—The scientific investigation of new or little known Indian and Colonial natural products with a view to their commercial utilisation throughout the Empire. The comparative examination with the same object of products of recognised value and importance, which, although known to occur or to be producible in India and the Colonies, are at present obtained commercially from other sources. Rendering advice and assistance to the Indian and Colonial Governments on all scientific and technical questions relating to the product, manufacture, and commercial utilisation of materials occurring throughout the British Empire. It was stated that the Indian Government had already made excellent preliminary arrangements for the exhibition of Indian products at the Imperial Institute, and for their scientific examination and technical valuation in or through the Department. Attached to the Department is a staff of specially selected scientific and technical Referees, whose advice is obtained on subjects connected with their special branches, whilst members of the staffs of a number of scientific and technical institutions in this country have furnished advice and assistance in conducting special enquiries or in supplying special information. Among the Institutions named were the City and Guilds Central Technical College, the Royal College of Science, the Government Laboratories at Somerset House, the Royal Arsenal, Woolwich, and at the Royal Mint, St. Thomas's Hospital, the Pharmaceutical Society, the Royal Indian

Engineering College, Cooper's Hill, and the Clothworkers' Research Laboratory in the Dyeing Department of the Yorkshire College, Leeds. It is intended greatly to extend this system of external reference and co-operation, to include institutions in India and the Colonies, so that the Department may gradually be developed into an Imperial Bureau of Scientific and Technical Advice, and be the means of federating scientific and technical workers throughout the Empire. An account was given of some of the more important enquiries which have already been set on foot at the instance of the Governments of India and the Colonies. The comparative value of the Indian Coal deposits and of the Indian iron ores, the improvement of Indian opium for medicinal purposes with a view to its extended employment in this country and abroad, the examination and valuation of Indian and Colonial fibres, of Indian tanning materials and dyestuffs, of essential oils and perfumes produced in Victoria, the chemical examination and therapeutic trial of important Indian and Colonial medicinal plants, the examination and valuation of Indian and Colonial timbers. At the close of the lecture the laboratories were open for inspection, and a number of interesting exhibits illustrating the work of the department were on view.

SOME EXTENSIONS OF THE PLASTER OF PARIS METHOD IN BLOWPIPE ANALYSIS.*

By W. W. ANDREWS.

In the years 1883 and 1884 two papers were published by Dr. Eugene Haanel, of Victoria College, Cobourg, Ontario, now of Syracuse University, in the *Proceedings of the Royal Society of Canada*, in which he described the brilliant results he was able to obtain in the production of the Bunsen iodide films on the blowpipe support, then proposed for the first time; namely, thin tablets of plaster of Paris made by casting sheets three-sixteenths of an inch thick on panes of glass and scratching them, before hardening, with ruled lines, so that when set they would readily break into oblongs measuring two and one-half by one and one-quarter inches. The pure white and highly polished surface of these tablets, and its great power of condensing heated gases and exhibiting the true colours, the cheapness, thermal and hygroscopic properties of the tablets, the ease with which they may be prepared and carried, and the excellence of the results when the sublimed iodides, bromides, oxides, and sulphides are deposited as coatings upon them, make them an ideal form of support in blowpipe work.

A small pit is made at one end of the tablet somewhat larger than a pin's head, and in this the ore to be tested is heated. The oxide coatings are produced by heating the substance *per se*, the bromides by adding to the substance a drop of fuming hydrobromic acid, and the iodides by adding a strong solution of hydriodic acid (made by dissolving five ounces of metallic iodine in seven ounces of water, by passing a steady stream of hydrogen sulphide through the solution while the iodine is slowly added). All who have experimented with this solution will be ready to admit that it yields superb results, but though easily renewable when one is near a hydrogen sulphide generator it is very unstable, takes a long time to prepare, and is troublesome to carry.

In 1890 Mr. F. A. Bowman read a paper before the Nova Scotia Natural History Society, in which was described a search for a solid reagent to replace the hydrogen iodide solution. He found that potassium hydrogen sulphide or any alkaline sulphate, which does not yield a coating of its own, mixed with potassium iodide would do very well. He also found that micro-

cosmic salt and potassium iodide gave good results. This mixture is a favourite one with some blowpipe experts. Tin is the only metal in the three series of the periodic table, beginning with copper, silver, and gold, which does not yield a characteristic coating with this reagent.

The writer has not been able to find whether there have been any other reagents besides these seriously proposed. Plaster of Paris as a support is mentioned in Moses and Parsons' late work as an alternative to charcoal. This is, as far as known to the writer, the only standard work in which the colours of the films on the tablets are described.

In the rapid development of other methods in chemical work the blowpipe has fallen largely into disuse, and for many years, besides the work outlined above and that of Col. Ross and some valuable tests for individual elements proposed by Chapman, little or no advance has been made. There are two possible lines of future progress in blowpiping, one in the direction of increased power and simplicity, so as to make the method more valuable for the field work of the mineralogist, geologist, and prospector, and the other in the direction of increased range and delicacy until the dry way tests rival the delicacy and distinctiveness of the wet tests, as they surpass them in expeditiousness. It may not be amiss, therefore, to call attention to the instrument of Plattner and Berzelius, which, in its modern form as the hot-blast blowpipe, and with the new support and the new reagents and reactions now known to chemistry, is an instrument surpassed by the electric furnace only.

The cleanliness of the method here described, as compared with the charcoal method, and the quickness with which sure results can be obtained with very small amounts, should call the blowpipe back to the table of the chemist for preliminary and confirmatory tests, to class work as an accompaniment of the wet methods, and to the lecture table for the purposes of illustration. It is possible to detect five or six metals in presence of each other on one tablet. Many of the coatings are permanent, and are all renewable on re-heating with addition of a drop of the reagent, so that a set of tablets carefully labelled with a pencil forms a permanent record of a set of experiments. The value of this to the practical chemist and to the student need not be emphasised. It may be noted that blowpiping is so much of an art that new methods are seldom well enough practised by those who have become skilful in other methods to reveal their value.

The extensions of the plaster of Paris method here proposed are—A set of new reagents, which yield some new reactions which are of value in detecting elements in the presence of each other, notably gold and copper in very small amounts in the presence of all elements so far experimented with; arsenic, tin, and antimony in presence of each other; sulphur in the presence of selenium and tellurium, and chlorine, bromine, and iodine in the presence of each other; a new set of film tests which are found to be of great delicacy (the limits of delicacy are now being measured, it being found that gold, one part in one million, and copper, one part in four millions, are easily detectable); a change in the composition of the tablets which does away with the necessity for using platinum wire in the production of the coloured glasses with borax and metaphosphoric acid, these being formed on the tablets with a decided gain in facility and delicacy; and lastly, several new methods of handling the tablets themselves.

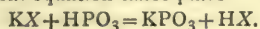
It is evident that solid reagents will always be the more convenient to carry afield, but in the laboratory liquids are to be preferred, since they are more readily applied, and when the assay is heated the reagent, which has soaked into the tablet, is fed steadily toward the hot portion of the tablet, so that the heated assay is constantly enveloped in the vapour of the reagent. For over two years the writer has used with satisfaction the following reagents, which have been selected from a score of

* From the *Journal of the American Chemical Society*, xviii., No. 10, October, 1896.

experimental ones. They are stable and almost odourless, can be carried to the field in a solid form and so used if need be, while a few seconds suffice to prepare them in liquid form if it be desired so to use them.

The chief reagent is a saturated solution of iodine in a strong solution of potassium thiocyanate in water. The solution takes place almost instantly and with great absorption of heat. The bottleful now in use has been in use for over two years, a little of one or other of the ingredients being added from time to time as seemed to be required. Exact proportions are not necessary to the efficiency of the reagent. It can be prepared on the field from the solid chemicals at a moment's notice. The brilliancy of the iodide films produced with this solution are not one whit behind those possible with the pure solution of hydriodic acid. Its coatings tend to form in definite bands of colour. The spheres of deposition of the iodide and the oxy-iodide are sometimes very well defined. Some striking and important variations are produced by the presence of the potassium thiocyanate, for example, with molybdenum, osmium, iridium, tin, antimony, lead, bismuth, cadmium, and mercury.

Dr. Haanel showed in his second paper that by means of hydrobromic acid, copper and iron could be detected at one operation in the presence of each other, and in the presence of nickel and cobalt and any other flux-colouring substances. Instead of the fuming acid with its dangerous properties, a mixture in molecular proportions of powdered potassium bromide and metaphosphoric acid, or potassium hydrogen phosphate or sulphate may be used. This, suggested by Bowman's work, suggests further a set of solid reagents, made by using potassium chloride, potassium fluoride, and potassium iodide with metaphosphoric acid, and these form a valuable set for special tests. They have the advantage of yielding at once the coloured flux and the coatings produced by any volatile matter in the assay. When heated the reaction represented by the following general equation takes place—



These two reagents, the iodine solution and the bromide mixture, suffice for the production of coatings. The following which are used to differentiate them, are dropped upon the oxide or iodide film and coloured spots are produced, or the colour is discharged to white (technically, *wiped*), or the coating disappears through solution and absorption by the tablet.

Dr. Haanel used ammonium hydroxide and yellow ammonium sulphide for the purpose of testing the solubility of the films and to produce the sulphide spots. Both of these are troublesome to carry, and the latter is objectionable on account of its intolerable odour, its instability, and the fact that for its renewal the hydrogen sulphide generator is required. It has been found that a solution of potassium sulphide, strong enough to show a clear amber colour, made by dissolving the solid potassium sulphide in water, or by boiling a strong solution of potassium hydroxide with an excess of flowers of sulphur till the solution assumes a blackish colour, which on cooling will be amber yellow, fulfils all the required conditions. If through the action of light it is decomposed, all that is necessary for its renewal is to boil the solution and perhaps add a little sulphur. We therefore have a reagent which can be carried as a solid, can be renewed anywhere, is as efficient as the ammonium sulphide solution, and is almost odourless.

In the place of ammonium hydroxide a solution of potassium cyanide is used, made a little more stable by the addition of a little ammonium or potassium hydroxide. Besides these the common acids of the laboratory are useful, and a solution of potassium thiocyanate.

The potassium thiocyanate solution is used in two ways. It is either dropped on the coating to test its solubility and to note the colours produced after heating, or it is dropped on the tablet before the coating is deposited, and then the hot vapours sweeping over the

moist spot give with some metals characteristic reactions.

Those coatings which are pure white, and therefore invisible on the white tablet, are examined on a tablet which has been smoked in a flame, or on one streaked up the middle by means of a glass rod which has been dipped in a solution of boric and metaphosphoric acids mixed with lampblack or bone charcoal. In this way the coatings may be viewed on a white and on a black surface at the same time.

In order that the coloured fluxes may be made on the tablets, the latter must be made more resistant to the dissolving effect of the metaphosphoric acid and the alkali in the borax. If one teaspoonful of boric acid be added to each quart of the water used in making the tablets, they will be found to be denser and to have the necessary quality. Borax can be fused on them without gathering any impurities from the plaster, and if metaphosphoric acid be substituted for phosphor salt, we have a flux which will spread upon the tablet and exhibit the colours of all degrees of saturation at the same time. This reagent, first proposed by Ross, who described its reactions, is preferable to microcosmic salt, since, as it contains no volatile matter and melts readily to a clear glass, it will show by effervescence the presence of water or carbon dioxide, or other gas in a mineral. With cobalt it yields a fine violet when cold, which becomes blue on the addition of any of the alkali metals, for which, therefore, it furnishes a ready test. The only objection to this reagent is the tendency of the sticks to deliquesce, but a piece can be kept in a corked test-tube,* which can be readily dried over the flame, if dampness should gather. In dry weather it causes no trouble. Its solvent power is very great, and the colours are fine. Ross asserts that silica and zirconia are the only oxides which are not soluble in this flux. The whole operation may be completed in the time usually required to form the bead in the platinum wire loop, and the volatile oxide films will be found on the tablet above the glass, where they may be tested with potassium sulphide and the other reagents. One operation, therefore, suffices for the determination of the volatile acid elements, the volatile metal or metals, and flux-colouring metal. Metaphosphoric acid well replaces potassium hydrogen sulphate in the operation as described in most text-books for the detection of carbon monoxide, carbon dioxide, iron, chlorine, bromine, iodine, nitrogen tetroxide, chlorine tetroxide, sulphur dioxide, hydrogen sulphide, hydrocyanic acid, and acetic acid.

(To be continued).

THE PURITY OF LONDON WATER.

At a recent meeting of the County Council the recommendation of the Water Committee that the Council's chemist should make three examinations weekly, for a period of six months, of the water supplied by each of the London water companies was adopted, though not without considerable discussion. In view of the expenditure of the ratepayers' money thus authorised, it may be interesting to consider briefly some of the results obtained by the Council's chemist and by other chemists employed on its behalf during last year, when a series of examinations similar to those now ordered was carried out. These results are contained in a large pamphlet, elaborately provided with tables and diagrams, which was ordered to be printed in May last and has recently been issued.

The general position adopted by Mr. Dibdin, the Council's chemist, in this report is that the examinations now regularly conducted by Dr. Frankland, the official analyst, and by the two eminent chemists employed on behalf of

* In this laboratory each student is supplied with a set of very small dipping tubes and a wooden block, into which holes are bored for the reception of a set of test-tubes closed with paraffined corks, to hold the reagents.

the companies, are incomplete, and therefore misleading. The incompleteness appears to consist in the fact that Dr. Frankland either ignores altogether, or else does not show in a manner satisfactory to the Water Committee, the amounts of suspended matter contained in the water, while the companies' chemists systematically write the word "None" in the column of their reports provided for the record of the suspended matter. The Council's chemist, on the other hand, contends that improved methods have enabled him to detect and measure a substantial amount of suspended matter in the filtered water supplied to consumers. Further, he holds it proved that the quality of the filtered water varies directly as that of the river water at the intakes near Sunbury, and considers it established that the existing arrangements for purifying the water are inadequate, particularly during periods of storm.

To take the second point first, Mr. Dibdin's conclusion is scarcely borne out by the facts and diagrams he himself supplies. According to the report the *maximum* quantity of suspended matter found at the beginning of the inquiry last year was 0.038 grains per gallon in the Southwark Company's water, there being 0.014 in the Chelsea Company's, and a little less in the Lambeth Company's, while the West Middlesex, New River, and Kent Companies' supplies contained from 0.004 to 0.002 grains per gallon. But towards the end of the inquiry, when the unfiltered water in the river was at its worst, none of the companies' supplies contained more than 0.006 grains, the average being 0.003. These statements, though they are Mr. Dibdin's own, do not altogether agree with the diagram he gives at the end of the book; they appear to prove, if they prove anything, that, so far from the filtration processes employed being inadequate during storm periods, it is precisely at storm periods that they are most efficient. This conclusion, it may be remarked, is probably not true in fact, but as it follows naturally from Mr. Dibdin's figures, it is not calculated to promote complete confidence in his methods and results.

Then as to the offending word "None" used by the companies' chemists. It must be remembered that purity in a chemical sense is entirely a relative term. It may almost be said that an absolutely pure substance is not known and has never been obtained. When a chemist pronounces a material pure he always speaks with reference to the use to which it is to be put. A substance, for example, which might fairly be designated pure if intended for use as an artificial manure, might be impure for the purposes of a chemical manufacturer, just as one reckoned pure for experiments in a school-laboratory would be quite worthless to the chemist engaged in the finest analytical work. So in the case of the suspended matter in London water. By the word "None" the chemists do not intend to imply its complete absence; they only mean to express their opinion that in view of the purposes for which the water is to be employed the amount of matter it holds in suspension is so small that it may safely be disregarded. A short scrutiny of Mr. Dibdin's figures will be enough to convince most people that the chemists are quite justified in their statement. According to him the average amount of suspended matter supplied during the year 1895 by the three companies that show the best results was 0.0011 grains a gallon. This amount he treats as an unavoidable *minimum*, and, using it as a sort of standard by which to judge other waters, deducts it from the 0.0033 grains which was the average quantity present in the water supplied by the five other companies. Thus he reaches the conclusion that these companies supplied in every gallon 0.0022 grains of avoidable suspended matter. This amount does not look very grand, so he proceeds to present the result in a way which makes it bulk more largely. Estimating that about 131 million gallons of river water are supplied to London daily, he calculates that in the course of a year nearly seven tons of chemically dry suspended matter, which

might be avoided, are distributed amongst Londoners by the water companies, or if the amount that is unavoidable be included about ten tons. But Mr. Dibdin would have the point put still more imposingly. He therefore adopts the expedient of adding 90 per cent of water to the dry matter, and is thus able to show that the people of London have supplied to them with their water the magnificent weight of 67.5 tons of avoidable "wet mud," or about 100 tons in all. If the computation of the supply of "wet mud" be made on the basis of the highest amount of matter found at any time during the year—viz., 0.0385 grains in the Southwark Company's water, Mr. Dibdin shows the result is 1145 tons, but he omits to add that were it made on the basis of the best water supplied by a company depending exclusively on the Thames the total would be about 15 tons of wet mud or 30 cwt. of dry matter.

The bacteriology of the water has also engaged the attention of the Council's chemist and those associated with him. Here, too, they have succeeded in obtaining results eminently satisfactory to themselves. They have found far more bacteria than did the official analyst and the companies' chemists, and their success inclines them to pronounce the latter's methods inadequate and their results untrustworthy. In explanation of the increased number of bacteria detected it is explained that, in the first place, the cultivations were made in such a way as to bring out all the microbes which will develop on a gelatine plate, instead of merely counting those which are self-evident in two days at ordinary temperatures, and, in the second place, that the samples were drawn from the companies' mains, not from the filter-wells and pumps. Of these two reasons probably the second is the more significant, though scarcely in the way Mr. Dibdin intends. The most elaborate bacteriological examination was carried out by Dr. Klein during eight weeks at the beginning of the year, but, unfortunately his results and those obtained in the Council's laboratory are not presented in such a form as to render comparison possible to any great extent. Dr. Klein's figures, however, in themselves are sufficiently puzzling. It is not quite obvious, for instance, why the number of bacteria present in 1 c.c. of water during one week should be 17,920 in one case, 16 in another, and 260 in a third, when all the three companies concerned draw their water from practically the same intake. Or take another question. Dr. Klein counted the microbes after three or four days' incubation in the first three weeks, but after only forty-eight hours in the last five. On the County Council theory that two days' incubation is not enough to develop anything like the full number of microbes, one would expect the average number of microbes present weekly in all the companies' waters to be greater in the first three weeks than in the last five. But such is not the case; the average was highest in the seventh and eighth weeks, lowest in the second and fourth, while in the fifth and sixth there were more present than in the first.

A possible explanation of these anomalies and also of the sudden jumps which are found in the numbers of the bacteria from week to week—one company, for instance, jumps from 116 in one week to 48,512 in the next descending to 7424 in the next again—may be hazarded. Every bacteriologist knows that the utmost care is required in taking samples, if the results are to be of any value. The receptacles must be sterile, and precautions must be observed to prevent contamination while they are being filled. But it does not appear at all certain that the necessary precautions were observed by the County Council. Dr. Klein, who did not collect his own samples, mentions that the water he examined was sent to him in large ordinary stoppered bottles, which are certainly not the kind of apparatus usually employed in delicate bacteriological investigations. If it should be the case that a County Council workman was simply sent to fill a number of these bottles from convenient stand-pipes according to his own lights, and without strict

measures being taken to insure sterilisation and prevent contamination, the curious results need no longer be a matter of surprise, any more than the discovery in the samples of "fragments of matter in a state of decomposition and swarming with various bacteria," or the occurrence of cotton fibres, &c. It does not militate against this suggestion that no correspondence can be traced between the numbers of microbes as stated by Dr. Klein and the efficiency of the filtration as measured by the amount of suspended matter indicated in Mr. Dibdin's diagram. Thus, according to the latter, the efficiency of the Chelsea Company's filtration remained unaltered for the third, fourth, and fifth weeks covered by Dr. Klein, yet the number of microbes he found in that company's water was 24,148, 2124, and 21,408 per c.c. for the three weeks respectively. In the sixth week the filtration became very much worse, and only began to improve again after the eighth week. Yet Dr. Klein's figures for these bad weeks are 264, 15,264, and 420 respectively. In the fourth week the Southwark Company's filtration began to deteriorate, but the number of microbes found by Dr. Klein was much less than in the preceding week. In the fifth week the filters were still worse and the microbes more numerous. But in the sixth week, while the filters had not improved, the number of microbes was barely one-twentieth of the figure for the week before.

Nor is confidence in the Council's bacteriology increased by the disagreement between the results handed in by the various investigators it employed. Drs. Klein and Stevenson, for instance, appear to have carried on investigations on samples supplied by Mr. Dibdin during the same period, from December 27, 1894, to February 21, 1895. Yet Dr. Stevenson reports that during those eight weeks there were never more than 200 micro-organisms present in 1 c.c. of the Kent and West Middlesex waters, while Dr. Klein only in two weeks found less than 200 in the same waters; in every other week the number exceeded 500, and thrice, according to him, it rose to over 17,000.

A good many other criticisms might be passed on these documents printed by the Council, but enough has been said to show that the results and conclusions contained in them ought not to be blindly accepted without examination. Not only are they in many cases inconsistent with each other, but they are at variance with the deliberate opinions of some of the highest authorities of the day. Now that the Council has decided to spend more money in continuing these investigations it is to be hoped it will take measures to render its methods and results absolutely above suspicion.—*The Times*, November 10, 1896.

Appointments.—Dr. Thos. Ewan, Chief Assistant in the Chemical Department of the Northern Polytechnic Institute, has been appointed Research Chemist to the British Aluminium Company, in their works at Oldbury. Mr. H. Charles L. Bloxam, new Chief Assistant in the Chemical Department of the Goldsmiths' Institute, New Cross, has been appointed to succeed Dr. Ewan at the Northern Polytechnic.

Society of Arts.—The opening meeting of the 143rd Session will be held on Wednesday evening, November 18th, at 8 p.m., when an Address will be delivered by Major-General Sir Owen Tudor Burne, K.C.S.I., C.I.E., Chairman of the Council. The subject of the Address will be "India, its Arts, Manufactures, and Commerce." At the subsequent meetings before Christmas, the following papers will be read:—"Recent Developments in Mechanical Road Carriages," by W. Worby Beaumont, M. Inst. C.E.; "The Teaching of Economics," by W. A. S. Hewins, M.A.; "Mining at Great Depths," by Bennett H. Brough, Assoc.R.S.M.; "The Chamber Music of Purcell, Handel, and Bach" (with illustrations on the original instruments for which it was written), by Arnold Dolmetsch.

CORRESPONDENCE.

CHEMICAL EDUCATION IN ENGLAND AND GERMANY.

To the Editor of the Chemical News.

SIR,—I have been much interested lately in the articles in the *CHEMICAL NEWS* relating to the question of why Germany stands so prominently before the world as a leader in both theoretical and practical chemistry. This question is an important one to Americans as well as Englishmen, and I, for one, should like more light on the matter. It is a fact that here in America, to the best of my knowledge, the rank and file of the chemical profession are very badly paid.

I hope that we are making a campaign of education here,—that is, educating the employer to realise the value of research work and pay for it. I look upon the chemist who is capable of original work as the man we should seek to produce in our schools, and who ought to be paid for his ability afterward. To me it seems that most employers make their mistake in employing a man of limited education for any except the roughest work. It is continually impressed on me that even the most unskilled work in a laboratory ought to be closely supervised by a man of intelligence and originality. Valuable suggestions are constantly coming to an educated man from the most unlikely sources. I do not mean to state that I think employers should engage men at high prices for routine work; but I do mean to say that a well-paid man, who has time to closely supervise all work done under his care, is a paying investment. In other words, we must have competently educated men.

It is a question in my mind whether our schools and colleges produce such men in as large numbers as they ought, considering the time and money spent.

Sir Henry Roscoe strikes at the root of the matter when he says that the students come into the colleges and universities very badly prepared when compared with their German brethren. I should like to suggest that a discussion of this matter of chemical education be opened in the columns of your paper. What should be studied to produce the most efficient chemist? This question, it seems to me, has been too largely left in the hands of the teachers. With all due respect to them I think, as a class, they lack many ideas that practical chemists could give them. It seems to me that all chemists should consult together to produce what I might call a framework for a universal course in their branch of Science. The advice of every thinking chemist is needed to produce the desired result. The trouble with our chemical studies at present seems to be that they are devised by men who lack experience. This is necessarily so as long as one man's ideas and experience are used. To illustrate what I mean, I will assume that a man has graduated at some good university at home, and then followed it up with study abroad. This man enters, we will say, the iron business, and spends some years in that line. He finally decides to teach, and entering some college he maps out a course in chemistry. This course will almost inevitably be warped out of shape by his experience in the iron business. The man who had spent years in the fertiliser business would naturally lean toward the studies he found most valuable to him in his former work; and so on along the line. Be the business iron, lead, greases, dyes, drugs, paints, soaps, sugars, food-stuffs, or any of the other lines open to the chemist, I think, in almost every case, the judgment is influenced and the value of the course of study impaired by coming from a man who, at best, has been able to follow but a few lines of one great subject. The average chemical student has no certain line of work that he knows he will follow after he leaves college, or if he has he never knows how soon he may be called to extend his own branch to cover other lines of work.

Surely the devising of a course of study that shall put a chemist in the position to follow out for himself any branch of chemistry is something worthy of the best work of the best chemists. No student can expect to master any branch of his subject while in school; but it seems as if, in that time, he ought to have his work so arranged that he would be competent to pursue his work along any line he might be called upon to follow. This is not the case in several institutions that I know about, and I suspect the required conditions are met by very few anywhere.

A discussion of the most essential studies for a chemist's calling may seem more fitted for a periodical devoted to pedagogics; but I feel sure the place for it is in such a paper as the *CHEMICAL NEWS*, that both practical and so-called theoretical chemists read. We need in this matter the best advice of each. Such a discussion could scarcely fail to be of profit to the whole profession.—I am, &c.,

A. C. BEEBE.

Savanna, Illinois, U.S.A.,
October 26, 1896.

THE DETERMINATION OF SULPHURIC ACID.

To the Editor of the *Chemical News*.

SIR,—In working out the process described (*CHEM. NEWS*, lxxiv., pp. 187—188) I find that, under certain conditions, there is a reversal of the reactions.

The affinities of the BaSO_4 , BaCrO_4 , and Ag_2CrO_4 seem so closely balanced that conditions of temperature, concentration of solution, or the mass-action of excess, as well as the sequence of the reagents, seem to determine whether one or other of the substances shall be formed or shall persist.

Further details will be submitted. Meanwhile I shall be glad to exchange observations with any reader who may have tried the process.—I am, &c.,

JAMES EDMUNDS.

29, Dover Street, Piccadilly.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 17, October 26, 1896.

The President opened the Session by announcing the death of Felix Tisserand, of the Section of Astronomy, who died on October 20th.

MM. Cornu and Sarrau were elected to join the Council for the improvement of the Polytechnic School.

Researches on Arabinose.—MM. Berthélot and G. André.—The authors conclude that under the influence of dilute acids arabinose gives rise to three orders of simultaneous reactions. 1. The formation of furfural by distillation, which differentiates the pentoses from the glucoses properly so-called. 2. The formation of humic acid, especially in closed vessels. 3. The slow formation of carbonic acid, especially marked on slow distillation.

Periodic Maxima of Spectra.—M. Aymonnet.—This paper will be inserted at some extent.

Hexamethylene-amine and some of its Derivatives.—M. Delépine.

Zeitschrift für Analytische Chemie.
Vol. xxxv., Parts 4 and 5.

A New Method for the Quantitative Isolation of Alkaloids suitable for Analytical Practice.—Dr. C. Kippenberger, Private Tutor in the Technical Chemical

Laboratory of the Federal Polytechnic College at Zurich.—This memoir will be inserted in full, if possible.

Application of Solutions of Iodine for the Volumetric Determination of Solutions of Alkaloids.—Dr. C. Kippenberger.

Contributions to a Knowledge of the Rancidification of Fats.—E. Spaeth.—Already inserted.

On Messinger's Method for the Determination of Acetone.—H. Ch. Geelmuyden.—This paper will be inserted if space permits.

A New Baryta Tube.—H. Ch. Geelmuyden.—This paper requires the accompanying figure.

Valuation and Standardising of Permanganate Solutions.—Prof. Dr. Riegler.—Already inserted.

Testing Bergamot Oil as to its Purity.—Prof. Dr. Arthur Bornträger.—A difference of opinion as to the possible composition of bergamot oil.

MEETINGS FOR THE WEEK.

WEDNESDAY, 18th.—Society of Arts, 8. Opening Address of the 143rd Session, "On the Arts, Manufactures, and Commerce of India," by Major-General Sir Owen Tudor Burne, K.C.S.I., C.I.E., Chairman of the Council.

THURSDAY, 19th.—Chemical, 8. "Mercury Hyponitrites," by P. H. Ray, D.Sc. "The Nitrites of Mercury, and the Conditions under which they are Formed," by P. H. Ray, D.Sc. "The Interaction of Mercurous Nitrite and the Alkyl Iodides," by P. H. Ray, D.Sc. "Crystallography of the Monohydrated Mercurous Nitrite," by T. H. Holland. "Sulphocamphoric Acid and other Derivatives of Camphorsulphonic Acid," by H. Lapworth, D.Sc., and F. Stanley Kipping, Ph.D., D.Sc.

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Foreman wanted for Ultramarine Factory, who thoroughly understands the manufacture, and is competent to erect plant of the latest type.—Address, with full particulars as to qualifications and salary required, to "Ultramarine," care of Deacon's Advertising Offices, 154, Leadenhall Street, London.

Wanted by a large Chemical Manufacturing Company, near New York City, New Chemical Products to Manufacture, and New or Improved Chemical Processes to introduce in its Works. All communications held strictly confidential.—Prof. Peter T. Austen, Polytechnic Institute, Brooklyn, N. Y., U.S.A.

FOR SALE.—THE CHEMICAL GAZETTE. Complete Set (unbound and uncut), 17 volumes; from November, 1842, to December, 1859.—Address, "Publisher," Chemical News Office, Boy Court, Ludgate Hill, London, E.C.

THE CHEMICAL NEWS.

VOL. LXXIV., No. 1930.

ANALYSIS OF AIR BY A MUSHROOM.

By Dr. T. L. PHIPSON.

In my notes on the "Origin of Atmospheric Oxygen," which have appeared in the CHEMICAL NEWS and the *Comptes Rendus* during the years 1893 to 1895, I have endeavoured to show, from palæontological considerations and direct chemical experiments, that oxygen gas—which at present forms about one-fifth of the volume of the Earth's atmosphere—has appeared progressively, as the result of the vital functions of green plants. At first, in the earlier ages of the globe, it was derived from the lowest order of plants (*Alga*), which, even in our day, give, weight for weight, more oxygen than the higher plants.

By causing various green plants to vegetate in nitrogen gas containing some carbonic acid, I became convinced that they are essentially anaërobic, that they can vegetate without free oxygen, that they were the means by which Nature has provided the atmosphere with free oxygen gas, and that, as the composition of the air gradually changed, becoming more and more oxygenated with the lapse of centuries, plants of aerobic nature and animals appeared.

If I place over water in a glass bell full of nitrogen containing some carbonic acid, a green plant such as *Convolvulus arvensis* or *Lysimachia nummularia*,* for instance, soon the atmosphere of the bell will be proved to contain oxygen, and in a few months it will be even richer in oxygen than the external atmosphere.

In *Agaricus atramentarius*, on the contrary, we have the example of a plant (animal?) composed of aerobic cells which cannot vegetate without free oxygen, and which is capable of analysing the air as completely as does a stick of phosphorus.

Thus, if I place over water in a graduated glass bell full of air (that is, nitrogen containing some oxygen) one of these mushrooms (which is entirely plunged in the air, i.e., not in contact with the water), and expose it to the solar light as I did with my green plants, I soon remark a considerable condensation of water-vapour, and then all the oxygen is absorbed; the carbonic acid produced being dissolved in the water, the latter rises in the bell-glass. For instance, in a small bell-glass of 200 c.c. capacity, the level of the water, in a few days, will be 160 c.c., and remain there. The bell-glass contains then only nitrogen, and the mushroom will dry up in it, and can be preserved any length of time, for its vegetation has ceased. It is, in fact, mummified in nitrogen†.

If I immediately place a green plant, such as the *Lysimachia* already mentioned, alongside of the *Agaricus*, I find that in a few days the latter will sometimes recommence slowly to vegetate; but the green plant providing more oxygen than the mushroom can utilise, the level of the water will soon stand at 170 c.c., or 180 c.c. for instance.

These experiments, which were carried on in the Casa Mia

* Both these plants are very good for such experiments and save much time, especially the *Lysimachia*, which belongs to the family of the *Primulaceæ*, several genera of which are water-plants, and the *L. nummularia* itself—now cultivated in many gardens—requires a good deal of water to flourish luxuriantly. The English name of the plant is Moneywort.

† In Nature this *Agaricus*, as everyone knows, soon ends by resolving itself into a dark-coloured liquid, which has often been used as ink for writing. An old botanist once told me it formed an indelible ink; but I find that chlorine turns it pale brown and finally bleaches it. The colour is contained in the spores.

Laboratory during the months of September and October. I hope to continue next season. At present I only wish to note that an individual of *Agaricus atramentarius* will analyse the air in a few days as completely as will a stick of phosphorus; because this mushroom, with its aerobic cells, can only live in an atmosphere containing free oxygen, and instead of pouring oxygen gas into the air, as green plants do, it absorbs this gas, converting it into water and carbonic acid, almost exactly as does an animal; only with the latter, the analysis is not complete, the animal, as we all know, dying of asphyxia before all the oxygen is absorbed.

The Casa Mia Laboratory, Putney,
November 11, 1896.

SOME EXTENSIONS OF THE PLASTER OF PARIS METHOD IN BLOWPIPE ANALYSIS.*

By W. W. ANDREWS.

(Continued from p. 243).

Descriptive List of Reactions Obtainable on the Tablets.

COPPER *per se* yields with difficulty a coating of volatilised metal. With the iodine solution it yields a white iodide coating and an emerald green flame. The iodide treated with a drop of potassium sulphide gives with gentle heat a blackish grey, which is removed by greater heat. Potassium cyanide and nitric acid dissolve the sulphide; hydrochloric and sulphuric acids have no effect till heated, and then they remove the spot. Potassium thiocyanate applied to the coating has no effect till heated, when a grey spot is shown. Any part of the coating touched with the tip of the flame shows the emerald green flame (Haanel). Metaphosphoric acid glass is greenish-blue when hot and a fine robin's egg blue when cold. Metaphosphoric acid and potassium bromide yield a splendid reddish violet coating of copper bromide (compare osmium). The bromide plus potassium sulphide shows a brown, which if heated turns blackish and then green, not affected by sulphuric acid, but immediately destroyed by a drop of nitric acid.

Copper plus metaphosphoric acid and potassium chloride yields a yellow brown cupric chloride, which, if treated with a drop of potassium thiocyanate, gives a black ring, which, if heated, becomes a black spot. If, before the assay is heated, a drop of nitric acid be placed one-half inch from the assay, and a drop of potassium thiocyanate be placed above that, on heating a fine and very volatile blue-black coating is deposited far up the tablet. This blue-black is not affected by acetic acid, is wiped off by sulphuric acid slowly, and immediately by hydrochloric and nitric acid. The formula of this compound will be determined if some method be found by which it may be collected in quantity. (See chlorine.)

Silver gives *per se* a pinkish-grey coating, which, touched by the blowpipe flame (flamed), becomes mottled brown. Reduced globules are often shown. Metaphosphoric acid yields the same coating and a pearl-like glass. The iodine solution yields a pale yellow, paler when cold, and around the assay forms a black, which does not fuse into the tablet (compare lead). Flaming with oxidising flame yields a mottled brown anywhere on the tablet. This is a very delicate test, and as all other coatings are volatile, the flame drives them off and leaves the silver oxide. Potassium sulphide produces a spotted blackish brown, probably potassium silver sulphide, the analogue of ammonium silver oxide, for if treated with a drop of potassium cyanide it immediately disappears, but if it be first heated, the potassium cyanide has no effect. If only one-half of the sulphide spot be touched with the tip of the flame, and then the potassium cyanide be applied, the

* From the *Journal of the American Chemical Society*, xviii., No. 10, October, 1896.

untouched portion will disappear while the other half will remain. Potassium thiocyanate on the iodide wipes it off; when heated the spot turns black, which is not wiped off by potassium cyanide.

Gold is slightly volatile *per se*, and more so if a solution of iodine in potassium iodide be used as a reagent, and the result is a fine rose-coloured film of the metal. If potassium thiocyanate be present no volatility is noticed. Gold and the other elements which respond to the new tests will be the subject of another paper.

Zinc *per se* yields a white coating, not very volatile, and luminous yellow when hot. Potassium sulphide and potassium thiocyanate produce no visible change on zinc films. The iodide film is a white, which treated in any part with cobalt nitrate solution yields the well-known zincate of cobalt, which is quickly decomposed by a drop of nitric acid (compare tin). This reaction obtained in this way is decisive for zinc, as aluminum and silicon do not volatilise, and are therefore not present in the coating. In the metaphosphoric acid glass, zinc causes flashes of light and detonations (Chapman). Metallic zinc sometimes yields *per se* a black sublimate along with the white oxide (compare arsenic).

Cadmium *per se* yields one of the most beautiful of the oxide films, which consists of a rich brown with black farther away and somewhat iridescent near the assay. Acetic acid does not affect it; potassium cyanide dissolves it at once (compare cadmium sulphide). Potassium sulphide and potassium thiocyanate yield a scarlet when hot, and bright yellow cold. This cadmium sulphide is not affected by potassium cyanide, is quickly destroyed by nitric acid, less readily by hydrochloric acid, immediately by acetic acid (compare cadmium oxide), and is not affected by sulphuric acid (compare copper).

The iodide coating is white with well-defined borders, which is easily distinguished in the presence of other white coatings by the *per se* and sulphide reactions. In the assay and near it the sulphide reaction will be seen caused by the potassium thiocyanate in the iodine solution (see sulphur). In metaphosphoric acid cadmium acts like zinc, and yields at the same time its oxide coating beyond the glass.

Mercury gives *per se* a very volatile film of mercury snow, which, with a feather, may be swept into a globule. It is not affected by the other reagents.

The iodide coating is a splendid combination of scarlet, yellow, and velvety green. This is caused by the mixing of the green mercurous iodide with the scarlet and yellow forms of the mercuric iodide. The reactions of each kind of iodide may be obtained on the one tablet. The green and the scarlet are the stable forms into which the coating changes on standing. A drop of the reagent or some more of the vapour blown across the coating changes all into the scarlet form. With mercurous iodide, sulphuric acid gives a yellow spot (mercurous sulphate). Potassium hydroxide gives a black; so does ammonium hydroxide (iodomercuramine, $\text{NH}_2\text{Hg}_2\text{I}$), and potassium sulphide. With the mercuric iodide, sulphuric acid increases the amount of the scarlet, potassium hydroxide yields a white, as does ammonium hydroxide (iodomercuramine) and potassium sulphide, yield a white spot quickly turning black. The sulphide spot, strange to say, is partially dissolved in nitric and hydrochloric acid, while sulphuric acid turns it brownish. Potassium cyanide yields a black, and potassium thiocyanate a dark spot, and if heated both are wholly volatilised (compare lead, bismuth, and silver). Water has no effect on this coating (compare lead), nor have hydrochloric, nitric, or sulphuric acids. By the last the coating is not readily wetted.

Gallium has not been experimented with. Indium yields a pale yellow iodide coating and a blue flame.

Thallium *per se* yields a feathery brown with white farther away and a green flame (compare arsenic and tellurium). Potassium sulphide gives a terra-cotta brown spot with a black ring. Potassium cyanide and potassium thiocyanate have no effect upon it. The iodide film is an

egg yellow with a purple black veil farther away. Potassium sulphide gives a rich brown which potassium cyanide darkens. Hydrochloric acid discharges it slowly and yellow is left (compare bismuth and tellurium). Potassium thiocyanate has no effect on the yellow or the black till heated, when it yields a white (compare bismuth, tellurium, tin, and lead). Potassium cyanide dissolves the black, but has no effect on the yellow. Sulphuric acid has no effect. A drop of the reagent on the coating heated shows a spreading black and an orange ring.

Carbon yields a sooty coating, which comes better if sulphuric acid or metaphosphoric acid be used upon the assay. In the case of the carbonates, boric oxide or metaphosphoric acid yield an odourless effervescence (Ross, Chapman). Organic acids blacken the tablet when heated.

Silicon.—An interesting reaction given by the silicates, especially the hydrous forms, is being investigated. Chapman dissolves a silicate in boric oxide and then precipitates the silica by adding metaphosphoric acid.

Germanium will give a light yellow iodide film, but none has been on hand to experiment with.

(To be continued).

SOURCES OF ERROR IN VOLHARD'S AND SIMILAR METHODS OF DETERMINING MANGANESE IN STEEL.*

By GEORGE AUCHY.

(Continued from p. 215).

Volhard's Method.

THE fact brought out by working upon Stone's method, that titration in faintly acid (nitric) solution gives too high results led to the suspicion that the same was also true of Volhard's regular method (sulphuric acid solution). The following tests were made:—

TABLE V.

No.	Volhard, Zinc oxide added to coagulation.	Volhard, Zinc oxide in large excess.
490	0'49	0'39
490	0'49	0'39
490	0'49	0'39
490	0'49	0'49
476	0'51	0'46
507	0'49	0'44
483	0'45	0'41
503	0'45	0'41
471	0'41	0'38
289	0'42	0'40
289	0'42	0'40
493	0'51	0'44
505	0'50	0'46
155	0'58	0'49
155	0'58	0'56
289	0'42	0'41
153	0'66	0'64

Results of the first column were obtained by adding zinc oxide till the solution stiffened and the iron all precipitated. In the second column of determinations the zinc oxide was added in sufficient excess of this amount to make the colour of the precipitated iron a light brown. The differences in the results were supposed to be due to this fact, already noted in considering Stone's method,—that titration in slightly acid solutions gives too high results. But a suspicion arose that these differences might, in part at least, be due to manganese being mechanically carried down with the iron when the large excess of zinc oxide was used. The obvious test of this

* Journal of the American Chemical Society, xviii., No. 6, p. 493.

would have been to make gravimetric determinations in the samples used in the last table. But, unfortunately, there remained but very little drillings of each of the samples. So the next best thing was done, and a standard manganese sample was prepared, and the determinations of these samples of the last table made by the colour method; in each case making a number of tests and taking the average. Results:—

TABLE VI.

No.	Volhard. Zinc oxide to coagulation.	Volhard. Zinc oxide in large excess.	Colour method.
490	0.49	0.39	0.48
507	0.49	0.44	0.435
483	0.45	0.41	0.43
503	0.45	0.41	0.423
471	0.41	0.38	0.38
289	0.42	0.40	0.40
492	0.51	0.44	0.46
503	0.50	0.46	0.49
155	0.58	0.49	0.56

Showing that when the neutralisation with zinc oxide is carried only to the point of precipitating the iron the result will invariably be from 0.01 per cent to 0.05 per cent too high; while, on the other hand, if the zinc oxide be added in excess of this amount, the result may be too low, and very much too low, from the precipitation of the manganese with the iron. These points would have been more certainly and satisfactorily proved, however, had the comparison of the Volhard results been made directly with results by the gravimetric process instead of by the colour test. In the following table such comparisons with the gravimetric method—in a new lot of steels—are made, and confirm the conclusions drawn from the preceding table. In the second column of tests, the neutralisation was performed in a way not to precipitate the manganese. In the third column of tests neutralisation was purposely performed in a way most favourable to the precipitation of manganese with the iron.

TABLE VII.

No.	Per cent.	Excess of zinc oxide. The excess added after filtration of ferric oxide.	Excess of zinc oxide. Added suddenly to the iron solution.	Gravi- metric method.	Colour method.
451	0.56	0.51	0.51	0.52 (acetate)	0.53
452	0.46	0.44	0.44	0.43	0.435
453	0.46	0.46	0.37	—	0.425
454	0.47	0.47	0.44	0.46 (Ford)	0.45
493	0.51	0.46	0.44	—	0.46
456	0.45	0.41	—	0.41 (Ford)	0.43
466	0.54	0.49	—	0.485	0.49
481	0.48	0.45	—	0.455	0.46
153	0.66	0.64	—	—	0.64
000	1.30	—	—	1.25*	—

* Made by Williams, of Boston.

Insufficient neutralisation gives high results. Complete neutralisation suddenly gives low results. Here, then, is the explanation for the low result of Table III. (483); the ferric oxide precipitate had carried down some of the manganese.

The remedy is obvious. It is to carefully avoid an excess of zinc oxide at the time of precipitating the iron; adding the necessary excess to the aliquot part of the filtrate from the ferric oxide, taken for titration—filtering off the undissolved zinc oxide before titrating. But this procedure involves considerable extra work. And it does not seem necessary, if certain precautions be taken, to filter off the ferric oxide before adding the excess of zinc oxide. For it is reasonable to suppose that it is the sudden addition of the zinc oxide in excess to the rather concentrated solution that carries down the manganese.

If the iron be first precipitated carefully by the gradual addition of zinc oxide, avoiding an excess, we have seen that no manganese is carried down. If now, the solution be diluted, mixed, and the ferric oxide be allowed time to begin to settle, there seems no reason why the further addition of an excess of zinc oxide should then precipitate manganese. That it does not is evidenced by the preceding table, second column of results, last four results, which were obtained in this way. Also all of the determinations by Stone's modification in Table XI.

In the determination of the results of the third column of results in the preceding table, pains were taken to add the excess of zinc oxide as suddenly as possible; nevertheless, only three out of the five results are low, showing (as also do the results of Table VI.) that manganese is not invariably carried down by such a procedure. In Stone's modification the tendency to a precipitation of manganese with the iron seems less; for of the numerous results by that method (obtained before the necessity of any precaution in precipitating the ferric oxide was known) only one is low. But in both methods the neglect of the precaution to thoroughly neutralise with zinc oxide almost invariably gives results more or less above the truth.

(To be continued).

ON THE INVERSION OF SUGAR BY SALTS.*

No. II.

By J. H. LONG.

(Concluded from p. 238).

Ferrous Bromide.

SOLUTIONS of this salt were made by adding the proper amount of bromine to an excess of iron and water. A reaction soon begins, which is hastened by heat. Finally the solution is thoroughly boiled, which eliminates all free bromine and leaves the iron in the ferrous condition. It is then filtered into the cold sugar solution and is ready for use. A solution so made is practically neutral.

Experiment 22.

FeBr₂. 0.54 N.

In 250 c.c., 50 grms. of sugar + 14.58 grms. of bromide, A = 31.43.

t.	a.	z.	Log. $\frac{A}{A-z}$	$\frac{1}{t} \log. \frac{A}{A-z}$
0	23.13°	—	—	—
15	16.76	6.37°	0.09836	0.00655
45	9.76	13.37	0.24062	0.00534
75	6.07	17.06	0.33988	0.00453
105	4.00	19.13	0.40743	0.00388
165	0.68	22.45	0.54406	0.00329
285	-4.03	27.16	0.86691	0.00304
345	-5.60	28.73	1.06598	0.00309

Experiment 23.

FeBr₂. 1.04 N.

In 250 c.c., 50 grms. of sugar + 28.08 grms. of bromide, A = 29.50.

t.	a.	z.	Log. $\frac{A}{A-z}$	$\frac{1}{t} \log. \frac{A}{A-z}$
0	21.20°	—	—	—
15	13.60	7.60°	0.12938	0.00862
45	6.22	14.98	0.30785	0.00684
75	2.90	18.30	0.42060	0.00561
105	0.75	20.45	0.51317	0.00489
165	-2.70	23.90	0.72163	0.00437
285	-6.35	27.55	1.17979	0.00414
345	-7.50	28.70	1.56673	0.00454

The normal solutions here invert but little faster than the half normal. The rates in both cases diminish

* From the *Journal of the American Chemical Society*, xviii., No. 8, August, 1896.

rapidly from the start, but after the middle of the inversion become nearly constant, as was observed with the ferrous chloride. The first three of the solutions taken from the thermostat had to be filtered before polarising.

Ferrous Iodide.

A half normal solution was made by mixing 15.87 grms. of iodine with an excess of iron and water, in the usual manner. On complete disappearance of the iodine the solution was boiled and filtered into a cold sugar solution. Water was finally added to make the volume up to 250 c.c. The amount of sugar present is not sufficient to prevent some decomposition on heating, but, as in the other cases referred to, the turbidity at first noticed disappeared after longer warming in the thermostat. The first polarisations were made after filtering, and those later were made directly.

Experiment 24.

FeI₂. N/2.

In 250 c.c., 50 grms. of sugar + 19.37 grms. of iodide.
A = 32.03.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t}$ log. $\frac{A}{A-x}$
0	23.73°	—	—	—
15	17.45	6.28°	0.09478	0.00632
30	13.57	10.16	0.16571	0.00552
45	11.62	12.11	0.20627	0.00458
60	9.73	14.00	0.24956	0.00416
90	7.50	16.23	0.30690	0.00341
150	4.40	19.33	0.40176	0.00268
270	0.90	22.83	0.54177	0.00200
390	-2.80	26.53	0.76520	0.00196

In my former paper a preliminary experiment with ferrous iodide was described in which the coefficient appeared to be nearly constant and much smaller than here. The experiments are, however, not comparable, as in the former case the sugar solution was very strong, containing, in 250 c.c., 125 grms. of sugar. In such a solution the degree of dissociation of the iodide would be necessarily very different from that in a weaker solution. In the strong solution no separation of ferrous hydroxide or other compound appears, even on warming. A strong syrup is much more stable than a weak one, and the lower rate of inversion may be thus easily accounted for.

Cadmium Chloride.

One solution of cadmium chloride was tested as to its inverting power. It was made with a salt purified by several crystallisations at a low temperature, free from uncombined acid.

Experiment 25.

CdCl₂. 0.94 N.

In 250 c.c., 50 grms. of sugar + 42.958 grms. of chloride.
A = 29.71.

0	21.41°	—	—	—
15	12.80	8.61°	0.14862	0.00990
30	6.59	14.82	0.30001	0.01000
60	-1.33	22.74	0.62967	0.01049
90	-4.89	26.30	0.94015	0.01044
150	-7.70	29.11	1.69475	0.01129

The rate of inversion is about as rapid as with 0.002 N hydrochloric acid at the same temperature and same sugar concentration.

Lead Nitrate.

A single test was made with a solution containing lead nitrate. The salt was re-crystallised from a pure Schuchardt specimen and was weighed in proper amount directly.

The coefficient here is found to increase very rapidly, as was noticed by Walker and Aston in their experiments (*loc. cit.*), which were carried out with a half normal nitrate solution at 80°, but with a weaker sugar solution. The mean value they give from the results of polarisation

Experiment 26.

Pb(NO₃)₂. N/2.

In 250 c.c., 50 grms. of sugar + 20.65 grms. of nitrate.
A = 33.70.

t.	a.	x.	Log. $\frac{A}{A-x}$	$\frac{1}{t}$ log. $\frac{A}{A-x}$
0	25.40°	—	—	—
15	22.86	2.54°	0.03403	0.00227
45	17.38	8.02	0.11803	0.00262
75	12.10	13.30	0.21800	0.00284
135	2.28	23.12	0.50314	0.00372
195	-3.63	29.03	0.85831	0.00440
345	-7.70	33.10	1.74948	0.00507

at three intervals is 0.00159, but the inversion was not carried nearly to completeness, as in the above case.

The experiments given show in a marked manner the extreme variations in the value and constancy of the inversion coefficient, and the data obtained may be roughly tabulated as follows:—

Potassium alum	K constant.
Ferrous sulphate	„ increases slowly.
Ammonium ferrous sulphate	„ „ „
Zinc sulphate	„ „ „
Cadmium chloride	„ „ „
Manganous sulphate	„ „ rapidly.
Manganous chloride	„ „ „
Lead nitrate	„ „ „
Ferrous chloride	„ decreases
Ferrous bromide	„ „ „
Ferrous iodide	„ „ „

In the cases of the last three salts the values of K decrease very rapidly at the beginning of the heating, but become nearly constant later, finally, in fact appearing to increase a little. This behaviour seems to bear some relation to the stability of the salts in aqueous or weak saccharine solution. As was mentioned these ferrous halogen solutions became turbid in the thermostat, and the first three or four portions withdrawn in each case for polarisation had to be filtered. Later, the liquids became perfectly clear under the influence of longer heating.

During the turbid stage of the reaction, owing to the temporary separation of a trace of base in insoluble form, the amount of free acid present would be relatively increased, and would therefore greatly accelerate the speed of inversion. With the clearing of the solutions on longer heating the normal hydrolysis only would obtain and then the reaction should approach in regularity that due to the presence of a small constant amount of mineral acid.

It was mentioned that the solutions with ferrous sulphate and ferrous ammonium sulphate became likewise turbid on heating. But here the very slight opalescence persisted through the whole time of heating, and was perhaps greater at the end of the reaction than at the beginning. Other experiments also show in this respect a marked difference between ferrous sulphate and chloride. In my former paper I referred to solutions of these salts which had been used qualitatively. Portions of these solutions that had not been heated are still in existence. After standing eight months in the light I find that the chloride is practically clear, while the sulphate has become much changed. The bottle contains a decided flocculent precipitate. My former experiments with a strong solution seemed to indicate that at a temperature of 100° the first slight precipitate which forms disappears, but this is not true of the weaker solutions at 85°.

The slight precipitate of ferrous chloride and other halogen compounds being temporary, while that of ferrous sulphate is apparently permanent, we should expect just such irregularities in the speed of inversion as the experiments actually show. A solution of manganous sulphate with sugar becomes also slightly decomposed on heating, and the decomposition increases with the time

and temperature. At a temperature of 100° a solution of 50 grms. of sugar and 10 grms. of the sulphate in 100 c.c. become so dark that an exact polarisation is not possible, even after filtering. The solution in the present case is much less concentrated, but the precipitate is still marked and its formation is undoubtedly attended by the separation of a little free acid. We should therefore expect an acceleration in the rate of inversion as before.

These considerations do not aid us in explaining, however, the increase in K for manganous chloride, cadmium chloride, or lead nitrate. The solutions with these salts are clear and remain so throughout the reaction. In the case of manganous chloride it must be remembered that an almost complete loss of colour follows after heating. The pink fades, and in a few hours at the temperature of the thermostat becomes imperceptible in a small volume of the liquid. The colour is not restored by cooling. We have here evidently a reaction in which a change takes place in the form of combination of the manganese, with a necessary alteration in the degree of dissociation of the salt.

It is true, as already said, that most of the bases under consideration form compounds with the sugars, so that we should expect from this cause a slight disturbance at least in the apparent rate of inversion. Too little is known of the optical properties of these saccharose, dextrose, and levulose metallic compounds to say just what effect they would have on the rotation, but that they have some action is suggested by the results of some of the polarisations to determine the end-point in the inversion. This was usually found a little below the theoretical, -8.6° for a 200 m.m. tube, but in several cases it was found above after prolonged heating. This was also true of a solution of sugar with manganous chloride, which stood exposed to the light several months.

It must be remembered also that solutions of dextrose are easily oxidised, and those of levulose much more so. The dark colour often seen near the end of the reaction points to such a decomposition.

It will be recognised that a determination of the hydrolysis of many of the heavy metallic salts cannot be measured with great accuracy, because of these several disturbing influences, but a comparison of some little value in the above cases may be made by considering the results obtained at the beginning of the reactions in which the coefficient is an increasing one, and near the end of the reaction in cases where it decreased and then became nearly constant. By taking the mean of the first two values in the one case, and of the last two in the other, we obtain the second column of the table below as the most probable values of the coefficient for half normal solutions.

In the third column is given a calculation of the extent of hydrolysis of the salts, expressed in per cents of total salt present, and based on a comparison with hydrochloric acid acting in 0.001 normal solution at the same temperature and on same amount of sugar. This comparison is at best a rough one, assuming as it does complete hydrolysis of the acid, and neglecting the effect of the excess of undecomposed salts on the rate of inversion.

	K .	Salts hydrolysed in per cent.
Lead nitrate	0.00244	0.096
Manganous chloride.. ..	0.00095	0.035
Manganous sulphate	0.00052	0.020
Ferrous sulphate	0.00085	0.033
Ferrous ammonium sulphate..	0.00068	0.026
Zinc sulphate	0.00040	0.016
Ferrous chloride	0.00164	0.063
Ferrous bromide (0.54 N) ..	0.00300	0.109
Ferrous iodide	0.00198	0.078
Potassium aluminum sulphate, N/4	0.01835	1.440
Cadmium chloride (0.94 N) ..	0.01000	2.080

The amount of hydrolysis is small in all cases except those of the alum and cadmium chloride.

My thanks are due to Mr. S. R. Macy for much assistance in the experimental work of the above.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following are the abstracts of papers received during the vacation, and published in the *Transactions* :—

107. "Contributions to the Chemistry of Phenol Derivatives." By R. MELDOLA, F.R.S., G. H. WOOLCOTT, and E. WRAY.

In this paper the authors describe a number of new derivatives of phenol, pyrocatechol, guaiacol, &c., which have been prepared incidentally in the course of an investigation into the methods of synthesis of certain natural phenol derivatives, such as eugenol, safrole, &c.

4-Chloro-3-nitrophenol from the corresponding nitro-aminophenol by Sandmeyer's process. White needles, m.p. $126-127^{\circ}$. Benzoyl derivative, m.p. $96-97^{\circ}$. Acetyl derivative, m.p. $83-85^{\circ}$.

Diacetyl-o-aminophenol (o-acetaminophenyl acetate) prepared by heating o-aminophenol with excess of acetic anhydride and dry sodium acetate. White prismatic needles, m.p. $123-124^{\circ}$, or with $14H_2O$, m.p. $76-77^{\circ}$. The nitro-derivative, obtained by nitrating the diacetyl compound by a mixture of ordinary and fuming nitric acid, gives, on hydrolysis, 5-nitro-2-aminophenol (Friedländer and Zeitlin, *Ber.*, 1894, xxvii., 196).

2-Chloro-5-nitrophenol, obtained from the last nitro-aminophenol by Sandmeyer's process. White needles, m.p. $118-119^{\circ}$. Benzoyl derivative, m.p. $127-128^{\circ}$.

2-Bromo-4-nitro-6-aminophenol, obtained by reducing the bromodinitrophenol, m.p. $118-119^{\circ}$, of Laurent and Körner by means of ammonium sulphide. Whitish needles, soluble in hot water; becomes brown on exposure to air; m.p. $162-163^{\circ}$. Both acid and basic in properties. Acetyl derivative, m.p. 194° with decomposition, can be made to decompose at 204° by rapidly heating. Anhydro-base; by heating acetyl derivative with acetic anhydride, m.p. $146-147^{\circ}$. Methyl ether (bromonitro-o-anisidine), yellow needles, m.p. $120-121^{\circ}$. Diazoxide; yellow needles, decomposing point $152-153^{\circ}$.

2-Chloro-4-nitrophenol, obtained from 4-nitro-2-aminophenol (Laurent and Gerhardt, *Annalen*, 1850, lxxv., 68) by Sandmeyer's process. Benzoyl derivative, m.p. 135° . Acetyl derivative, m.p. 63° .

4-Nitro-2-aminoanisole, prepared by reducing 2:4-dinitroanisole in alcoholic solution with ammonium sulphide. Orange needles (from water), m.p. 118° . Acetyl derivative, m.p. $174-175^{\circ}$.

5-Nitro-2-aminoanisole, prepared by hydrolysing the acetyl derivative obtained by nitrating o-nitroacetanilide, (Mühlhauser, *Annalen*, 1881, ccvii., 242). Yellow needles (from water), m.p. $139-140^{\circ}$. Acetyl derivative, m.p. $145-146^{\circ}$.

Nitroaminoguaiacol, obtained by reducing dinitroguaiacol, m.p. 121° (Herzig, *Monatsh.*, 1882, iii., 825) with ammonium sulphide; brown needles, both acid and basic; decomposing point 182° . Acetyl derivative, decomposing point $224-226^{\circ}$. Diacetyl derivative, decomposing point 204° . Diazoxide; orange needles, exploding sharply at $169-170^{\circ}$. Constitution probably 4-nitro-6-amino-2-methoxyphenol.

5-Nitro-3-aminopyrocatechol, obtained by reducing the dinitropyrocatechol of m.p. 164° (Nietzki and Moll, *Ber.*, 1894, xxvi., 2183) with ammonium sulphide; acid and basic ochreous needles, m.p. $220-221^{\circ}$ with decomposition. Diazoxide; flat, golden needles, exploding sharply at $159-160^{\circ}$. Soluble in alkali, with a purple

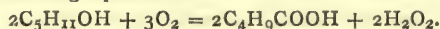
colour. The authors point out that generally the formation of diazoxides may be taken as evidence that the amino- and hydroxy-groups are ortho with respect to each other, and they consider the formula of the compound to be 5-nitro-3-amino-2-hydroxyphenol.

108. "*Action of Light on Amyl Alcohol.*" By A. RICHARDSON, Ph.D., and EMILY C. FORTEY, B.Sc.

The authors have investigated the action of light on a number of alcohols in presence of oxygen. The alcohols used were obtained from Kahlbaum, and carefully purified by re-distillation. It was found that whereas in the case of methyl, ethyl, propyl, and butyl alcohols an exposure extending over many months failed to produce any apparent change, the alcohols remaining neutral to litmus and containing no hydrogen peroxide, amyl alcohol gave strongly acid reactions and contained large quantities of hydrogen peroxide after only a few days' exposure. A similar change seemed to take place in the case of octyl alcohol, but to a very much smaller extent. The action of light on amyl alcohol was therefore studied in detail.

Amyl alcohol was exposed to light in presence of excess of water and of oxygen for a few days. A portion of the water was then tested with titanous acid, when the presence of hydrogen peroxide was shown by a deep brown colouration. Another portion was shaken with pure ether and potassium bichromate, when the ether assumed an intensely blue colour, leaving no doubt as to the presence of hydrogen peroxide in the solution. In another experiment liquid water was absent, amyl alcohol being exposed in presence of moist oxygen. Two days' exposure sufficed to bring about the formation of hydrogen peroxide, as shown by the titanous acid test. A third experiment was made with dry alcohol. A sample of amyl alcohol dried first from quicklime, then by distillation from sodium, was sealed in a bent tube containing oxygen and phosphorus pentoxide (care being taken not to allow the liquid to wet the pentoxide), and kept in the dark for seven weeks. After exposure, the alcohol was found to contain abundance of hydrogen peroxide.

The other products formed were then examined. The acidity was found to be due to the presence of valerician acid, and the absence of carbon dioxide leads to the conclusion that the change is one of a comparatively simple nature, not involving the breaking down of the molecule. It seems, then, that the products formed by the oxidation of amyl alcohol in presence of sunlight and oxygen only differ from those formed when other oxidising agents are used in that hydrogen peroxide is formed instead of water. The change may, therefore, be represented by the following equation:—



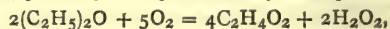
It was found that the presence of sunlight was essential to the change, a sample of amyl alcohol kept in the dark at 100° for nine days remaining neutral to litmus, and containing no hydrogen peroxide.

109. "*Note on the Action of Light on Ether.*" By A. RICHARDSON, Ph.D., and EMILY C. FORTEY, B.Sc.

Ether prepared from pure alcohol and pure sulphuric acid, and then treated with potassium bichromate, was dried by repeated distillation from phosphorus pentoxide in a specially constructed apparatus by means of which samples could be sealed for use without contact with air. The ether was then exposed in a tube containing oxygen which had been dried by contact with phosphorus pentoxide for many weeks. After three days' exposure the liquid gave a well-marked peroxide reaction when tested with titanous acid.

In order to investigate the other products formed, a sample of ether was exposed for many weeks in presence of water and oxygen. It was then rich in hydrogen peroxide, and gave an acid reaction with litmus. The neutralised solution was distilled on the water-bath. The distillate, consisting chiefly of ether, was also proved to contain aldehyde by its reducing action on ammoniacal

silver nitrate, and by its restoring the colour to rosaniline hydrochloride, decolourised by sulphurous acid. The residue in the distilling flask gave a distinct red colour with ferric chloride, and the characteristic smell of ethyl acetate on warming with alcohol and sulphuric acid, leaving no doubt as to the formation of acetic acid. No carbon dioxide was formed in the reaction, which may, therefore, probably be represented by the equation—



aldehyde being an intermediate product.

Here, again, hydrogen peroxide takes the place of the water which is formed when ordinary oxidising agents are used.

110. "*The Constitution of Lapachol and its Derivatives. Part III. The Structure of the Amylene Chain.*" By SAMUEL C. HOOKER.

Experimental proof is brought to show that the amylene chain must be written $-\text{CH}_2\cdot\text{CH}:\text{C}(\text{CH}_3)_2$, and not $-\text{CH}:\text{CH}\cdot\text{CH}(\text{CH}_3)_2$, as has been previously assumed. In accordance with this change, new formulæ are proposed for various lapachol derivatives.

111. "*Lomatol.*" By SAMUEL C. HOOKER.

The colouring-matter obtained by Rennie (*Proc.*, xi., 150) is a hydroxyisolapachol.

112. "*Contributions to the Knowledge of the β -Ketonic Acids. Part II.*" By SIEGFRIED RUHEMANN, Ph.D., M.A., and C. G. L. WOLF, B.A., M.D.

The authors describe the products of the action of ethylic chlorofumarate on ethylic benzoylacetate, and on the sodium derivative of ethylic methylacetoacetate; of the hydrolysis of ethylic methylfurfurandicarboxylate; and of the action of ethylic sodioacetoacetate on ethylic α -chlorocrotonate.

113. "*Formation of Pyrazolone Derivatives from Chlorofumaric Acid.*" By SIEGFRIED RUHEMANN, Ph.D., M.A.

The author describes the products of the action of hydrazine and phenylhydrazine on ethylic chlorofumarate. In the former case ethylic 5-pyrazolone-3-carboxylate is formed, identical with v. Rothenburg's compound (*Z. pr. Chem.*, 1895, li., 53), in the latter an ethereal salt of bis-phenylpyrazolonecarboxylic acid. Their properties are described.

114. "*Studies of the Terpenes and Allied Compounds. Note on Ketopinic Acid—a Product of the Oxidation of the Solid Hydrochloride (Chlorocamphydrene) prepared from Pinene.*" By HENRY E. ARMSTRONG.

The acid described has the formula $\text{C}_{10}\text{H}_{14}\text{O}_3$, and is obtained by the interaction of chlorocamphydrene and the strongest nitric acid. It melts at 234° (uncorr.), Baric, calcic, and methylic salts are described, as well as a hydrazone (m. p. 146°) and a hydroxime (m. p. 216°). Ketopinic acid appears to be a saturated ketomono-carboxylic acid.

115. "*Acid Compounds of Natural Yellow Colouring-matters. Part II.*" By A. G. PERKIN.

In a previous communication by Perkin and Pate (*Proc.*, 1895, ii., 126), it was shown that when treated with mineral acids in the presence of acetic acid, quercetin, rhamnetin, rhamnazin, fisetin, and morin yielded crystalline compounds, the formula of which is generally represented as an addition product of one molecule of acid to one molecule of colouring-matter. It has since been shown that luteolin and myricetin behave similarly, and there can be little doubt that all these colouring-matters belong to the so-called quercetin group. In this paper certain of these compounds not previously examined are described, viz., quercetin hydrochloride, $\text{C}_{15}\text{H}_{10}\text{O}_7\cdot\text{HCl}$; morin hydriodide, $\text{C}_{15}\text{H}_{10}\text{O}_7\cdot\text{HI}$; and luteolin hydriodide, $\text{C}_{15}\text{H}_{10}\text{O}_6\cdot\text{HI}$. It is also shown that whereas quercetin tetramethyl ether resembles the mono-methyl ether of rhamnetin in reacting with sulphuric acid, and not with the haloid acids, dibromo-quercetin

and tetrabromo-morin yield no compounds with mineral acids. The other known members of the quercetin series are dioxyflavone (Friedländer and Rudt, *Ber.*, 1896, 878) and chrysin, the colouring-matter of poplar buds. The former has been shown by its discoverers to yield acid compounds, but, on examination, the latter was found to be devoid of this property. Various members of the ketone group (gallacetophenone, alizarine, and maclurin), of the xanthone group (gentisin, euxanthone, datiscetin), and of the anthraquinone group, were examined in this respect, but yielded no compounds with mineral acids. Catechin and kinoin also, the latter a constituent of malabar kino, did not react.

For the constitution of the acid compounds two schemes are put forward, the first a similar one to that suggested by Nietzki and Schröber (*Ber.*, 1895, 50) for the phthaleine salts, and a second depending upon the saturation of the ethylene-bond in the γ -pyrone ring.

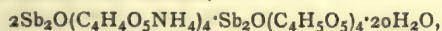
It is considered probable that this reaction is characteristic of the quercetin group, and will thus be of service for distinguishing its members from the other classes of non-nitrogenous, yellow, mordant dye stuffs which are at present known to exist.

116. "Studies on Citrazinic Acid." Part IV. By W. J. SELL, M.A.

The author has employed Tiemann and Reimer's reaction (*Ber.*, 1876, ix., 423, 824) to introduce the aldehyde group into hydroxyl derivatives of pyridine, and has isolated and analysed the disodium salt of the monaldehyde of citrazinic acid, the monaldehyde acid, the oxime of the monaldehyde acid, and the phenylhydrazine salt of the hydrazone.

117. "The Action of certain Acidic Oxides on Salts of Hydroxy Acids." III. By G. G. HENDERSON, D.Sc., M.A., and JOHN M. BARR.

By the prolonged boiling of antimonious oxide in an aqueous solution of the primary malate, ammonium antimonio malate was obtained,



resembling the potassium salt already described (*Trans.* 1895, 1030). It forms large colourless crystals, easily soluble in water, and decomposes when heated to about 115° , or when its aqueous solution is boiled for a short time, except in presence of excess of the oxide.

Antimonious oxide dissolved slowly in a boiling solution of sodium hydrogen malate, and, on adding alcohol, a syrup was precipitated, which consisted principally of the sodium compound. However, the pure salt could not be obtained in a crystalline condition.

While arsenious oxide dissolved freely in solutions of primary sodium and ammonium malates, salts corresponding to the antimonio-malates could not be prepared in a pure state, owing to the instability of the products, although an impure ammonium compound was obtained.

Ammonium antimonio-mucate, $\text{SbO}(\text{NH}_4)_4\text{C}_4\text{H}_8\text{O}_8 \cdot 3\text{H}_2\text{O}$, was prepared by prolonged boiling of the oxide with a solution of the primary mucate and repeated re-crystallisation of the product. It is a white, finely crystalline powder, sparingly soluble in cold, but fairly easily soluble in hot water. In its other properties it closely resembles the potassium salt already described (*loc. cit.*). The sodium salt, $\text{SbONaC}_4\text{H}_8\text{O}_8 \cdot 3\text{H}_2\text{O}$, prepared similarly, is also a white crystalline powder, only differing from the others in its greater solubility in water. On addition of barium acetate to a solution of the sodium salt, what appeared to be a slightly impure barium salt was gradually precipitated in the form of a white powder.

Attempts to prepare arsenio-mucates of sodium and ammonium were not successful, and failure also attended our efforts to obtain compounds of the alkali salts of mandelic acid with antimonious and arsenious oxides respectively.

Salicylic and gallic acids were then taken as examples of phenol acids, but experiments showed that neither

antimonious nor arsenious oxide entered into reaction with any of the alkali salts of these acids.

Molybdenum trioxide was found to dissolve in boiling aqueous solutions of primary tartrates, forming compounds with them. Sodium molybdi-tartrate,—

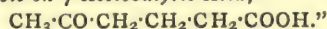


was obtained in the form of a white crystalline powder, easily soluble in cold water, and decomposed on exposure to light or to a temperature of 90° , and also when its aqueous solution is boiled for some time. The potassium salt is also a crystalline powder, very similar in properties to the sodium salt, but less stable. The ammonium salt was only obtained in the form of a gelatinous precipitate.

Sodium tungsti-tartrate, $\text{WO}_2(\text{NaC}_4\text{H}_4\text{O}_6)_2 \cdot 5\text{H}_2\text{O}$, was prepared by dissolving tungsten trioxide in a boiling aqueous solution of the primary tartrate, excess of the latter being used. It crystallises in white plates, easily soluble in water, and decomposed when heated to about 110° , or when its aqueous solution is boiled for any length of time. The potassium salt, $\text{WO}_2(\text{KC}_4\text{H}_4\text{O}_6)_2 \cdot 4\frac{1}{2}\text{H}_2\text{O}$, and the ammonium salt are also crystalline, the former closely resembling the sodium salt in properties, the latter being very unstable in presence of water. The barium salt, $\text{WO}_2(\text{C}_4\text{H}_4\text{O}_6)_2\text{Ba}$, is precipitated as a white insoluble powder when barium acetate is added to a solution of the sodium salt.

Silicon dioxide, used in the form of gelatinous silicic acid, apparently does not react directly with primary tartrates, but titanium dioxide dissolves in solutions of these salts, yielding substances which are being examined. It remains to be tried whether other acidic oxides also react with tartrates and salts of other hydroxy-acids.

118. "Note on γ -Acetobutyric Acid,—



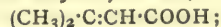
By W. H. BENTLEY and W. H. PERKIN, Jun.

The properties of this acid were carefully investigated in order to enable the authors to compare it with a ketonic acid obtained from sulphocamphyllic acid. It was prepared by the hydrolysis of ethylic acetyl glutarate (Wolff, *Annalen*, 1883, ccxvi., 129), the method of preparation being improved in some respects.

The oxime (m. p. $104-105^\circ$) and the semicarbazone (m. p. 174°) are the most characteristic derivatives; when oxidised with nitric acid, aceto-butyric acid yields succinic acid.

119. "Some Derivatives of Propionic Acid, of Acrylic Acid, and of Glutaric Acid." By W. H. PERKIN, Jun.

This paper describes in the first place the results of the investigation of dimethylacrylic acid,—



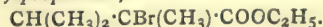
trimethylacrylic acid, $(\text{CH}_3)_2\text{C}:\text{C}(\text{CH}_3)\cdot\text{COOH}$; and *isopropylacrylic acid*, $(\text{CH}_3)_2\text{CH}\cdot\text{C}(\text{CH}_3)\cdot\text{COOH}$.

The ethereal salt of the former acid, when digested in alcoholic solution with the sodium compound of ethylic malonate, yields ethylic dimethylpropanetricarboxylate, $(\text{COOC}_2\text{H}_5)_2\text{CH}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$ (compare Auwers, *Ber.*, 1895, xxviii., 1130; *Annalen*, 1896, ccxcii., 145), (b. p. 203° , 60 m.m.), from which, by hydrolysis and elimination of carbon dioxide,—



$\beta\beta$ -dimethylglutaric acid, was obtained. This acid melts at 101° , and gives an anhydride melting at 124° and an anilic acid melting at 134° .

Trimethylacrylic acid, together with *isopropylacrylic acid*, results from the action of alkalis on ethylic α -bromo- $\alpha\beta$ -trimethylpropionate,—



The former is a crystalline compound which melts at $70-71^\circ$, and from which the following derivatives have been prepared.

$\alpha\beta$ -Dibromo- $\alpha\beta\beta$ -trimethylpropionic acid,—
 $\text{CBrMe}_2\cdot\text{CBrMe}\cdot\text{COOH}$

(m. p. 188°).

β -Bromo- $\alpha\beta\beta$ -trimethylpropionic acid,—
 $\text{CBr}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\text{COOH}$

(m. p. 88°).

β -Iodo- $\alpha\beta\beta$ -trimethylpropionic acid,—
 $\text{CI}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$

(m. p. 88°).

When the mixed ethereal salts of trimethylacrylic and isopropylacrylic acids (as obtained by the action of quino-line on ethylic α -bromotrimethylpropionate) are digested with the sodium compound of ethylic malonate, the ethylic isopropylacrylate only enters into the reaction with formation of ethylic isopropylpropanetricarboxylate, $(\text{COOC}_2\text{H}_5)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{COOC}_2\text{H}_5)_2\cdot\text{CH}(\text{CH}_3)_2$ (b. p. 208–210° at 45 m.m.), the ethylic trimethylacrylate remaining apparently unattacked.

$(\text{COOH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{COOH})_2\cdot\text{CH}(\text{CH}_3)_2$,

isopropylpropanetricarboxylic acid, crystallises in colourless needles, which melt at 265° with decomposition into carbon dioxide and isopropylglutaric acid,—

$\text{COOH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{COOH})\cdot\text{CH}(\text{CH}_3)_2$.

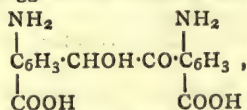
This acid melts at 95°, and gives an anhydride at 53° and an anilic acid melting at 158–159°; its constitution is proved by its synthesis from ethylic isopropylmalonate and ethylic β -iodopropionate.

This paper contains also an account of a number of experiments on the action of phenoxyethylbromide, $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, on the sodium compounds of ethylic dimethylpropanetricarboxylate and ethylic isopropylpropanetricarboxylate.

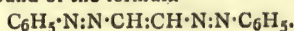
120. "On the Action of Chloroform and Potash on Metamidobenzoic Acid." By W. J. ELLIOTT, M.A.

By the action of aqueous potash and chloroform on metamidobenzoic acid, a compound is obtained which is insoluble in all solvents, reduces Fehling's solution, and gives with phenylhydrazine a red compound, which is not a hydrazone, but has the properties of an azo-compound.

The compound has the empirical formula $\text{C}_8\text{H}_7\text{NO}_3$, and the author suggests the constitutional formula—



that is di-amido-di-carboxy-benzoin. When boiled with water for some time, the compound is oxidised, yielding a solution of metamidobenzoic acid. With phenylhydrazine, metamidobenzoic acid and a compound having the empirical formula $\text{C}_7\text{H}_6\text{N}_2$, are formed. The author suggests the formation of an osazone, which is reduced, by the hydrogen set free, to metamidobenzoic acid and a disazo-compound of the formula—



PHYSICAL SOCIETY.

Ordinary Meeting, November 13th, 1896.

Captain ABNEY, President, in the Chair.

A PAPER "On some Experiments with Röntgen's Radiation," by Prof. THRELFALL and Mr. POLLOCK, was, in the absence of the authors, read by the Secretary.

The authors describe a form of Crookes's tube which, while it can be made by anyone capable of the most elementary glass-blowing, gives a plentiful supply of Röntgen rays. The results of their experiments may be summed up as follows:—

(1) The Röntgen radiation does not consist in the projection of gaseous matter, or, if it does, the amount of such matter involved is extraordinarily small.

(2) The Röntgen radiation does not consist in the projection of æther streams having a velocity above a couple of hundred metres per second: this is true whether the radiation takes place in air or in benzene.

(3) The properties of the æther, regarded as determining the velocity of electro-magnetic waves, are not greatly changed (*i.e.*, not at all within our experimental limits) by the Röntgen radiation, and this applies alike to the æther in air and in benzene.

(4) A selenium cell, composed of platinum electrodes and highly purified selenium, is affected by Röntgen radiation to an extent which is comparable with the effect produced by diffused daylight.

(5) No permanent or temporary electromotive force is set up in a selenium cell by the Röntgen radiation.

The authors have come to conclusion (1) by exposing an exhausted tube placed in parallel with a spark-gap so adjusted that the spark just passes over the gap rather than through the tube to the Röntgen radiation. They find that a vacuum tube in parallel with a spark-gap is very sensitive to changes in pressure within the tube. Conclusions (2) and (3) were arrived at by using Michelson's arrangements for the interference of two beams of light.

Mr. SHELFORD BIDWELL said he had made some experiments on the effect of Röntgen rays on the resistance of selenium, but with a negative result, although he could have detected a much smaller change than that found by the authors. It might be that this difference was due to the tube, for in his experiment the radiation started from a platinum plate within the tube, while in the authors' arrangement the radiation starts from where the cathode rays strike the glass of the tube.

Prof. SILVANUS THOMPSON said there were a number of points with reference to the Röntgen radiation which required clearing up. For instance the suggestion that they were vortices in the æther had not been tested. Again, LaFay says that if the rays are passed through a metal screen which is charged with electricity, then the rays can be deflected by a magnet. He (Prof. Thompson) had not been able to repeat this experiment, neither had he that of Galitzine on the polarisation of the rays by tourmaline. The statement of Prof. J. J. Thomson, that under the influence of the radiation paraffin became a conductor, had not been satisfactorily proved. As to the wave-length, while some observers obtained values about one-tenth that of the extreme violet, another had obtained a value greater than that of the extreme red. He (the speaker) did not understand the authors' device for detecting changes in the vacuum of a tube, since everyone who has worked with Crookes's tubes has found that the resistance is always greater for a spark in one direction than in the other, and also varies with the battery power employed. Lenard, adopting Hertz's arrangement, uses as anode a cylinder surrounding the cathode (a disc), the idea being that by using such a symmetrical arrangement the cathode radiation was more homogeneous. It might be advisable, when seeking to produce homogeneous Röntgen rays, to adopt such a symmetrical arrangement.

The CHAIRMAN said that since no selection was made with reference to the announcements which appeared in the *Comptes Rendus*, it was frequently found that these announcements turned out to be wrong.

Mr. BRYAN then read a paper, by himself and Dr. BARTON, "On the Absorption of Electrical Waves along Wires by a Terminal Bridge."

The authors employ, for the generation of the oscillations, an arrangement of the same description as that used by Bjerknes, the waves being propagated along two parallel wires about 116 m. long. In order to measure the waves, they use a small electrometer with an uncharged needle. The resistances employed to form the

bridge consist of pencil-marks on ground glass. Bridges of three resistances have been examined, one having as nearly as may be the resistance necessary, according to Heaviside's theory, to give complete extinction of the reflected wave, and of the others one was of higher and the other of lower resistance. In each case the results confirm the theory, and it is thus experimentally proved that, by using a bridge of this description, the reflected train of waves can be completely extinguished.

Mr. BLAKESLEY asked if the authors had made any allowance for the capacity of the wires.

Mr. CAMPBELL asked if the resistances given were expressed in ohms or in electro-magnetic units.

Mr. BIDWELL asked if the authors had found that the pencil-trace resistances obeyed Ohms' law. He found that if you balance with one cell in the battery circuit, then, on increasing the battery power to two cells, the resistance alters.

Mr. APLEYARD suggested that the variation was caused by the contacts at the ends not being good.

Mr. CAMPBELL said the same variation occurred in the case of mixtures of clay and plumbago where the contacts could be made quite good.

Mr. CARTER suggested electroplating the ends to give good contact.

Mr. BRYAN, in his reply, said that they had not considered the question of capacity, and that in their case they did not require to know the resistance very accurately.

The Society then adjourned till November 27th.

NOTICES OF BOOKS.

The Energy of Living Protoplasm. By OSCAR LOEW, Ph.D., Professor in the Imperial University, Japan. London: Kegan Paul, Trench, Trübner, and Co., Ltd. 1896.

THE author has come to the conclusion that there must exist an unstable modification of albumen with which alone we have to do in living protoplasm, and differing from that of dead protoplasm or from ordinary protoplasm, though easily passing into the latter. He declares that the electrical phenomena observed are like animal heat, mere secondary actions and not the first cause of life. He quotes Liebig (*Chemische Briefe*, xxiii., 1858) as defending energetically the doctrine of a specific vital power. Reil, Schleiden, Matteucci, and Lehmann all protest more or less against this vitalistic hypothesis. Tyndall's celebrated dictum that we have in matter the "promise and potency of every form and quality of life" is, it is here pointed out, merely the re-issue of an old thought of Francis Bacon "De princip. atque origg." (*Opera ed. Bohn*, ii., 691).

We find here honour awarded to a man who is generally overlooked by his own countrymen. We are reminded how Dr. Mayow showed "that life and fire are sustained by one and the same principle contained in the air, and that this principle is mixed with another indifferent substance. He can be considered not only as a forerunner of Lavoisier, but also as the first propounder of the doctrine of the conservation of energy."

But passing over not a few such significant utterances we come to the main passage in which Professor Loew sums up his facts:—

1. The transition of living protoplasm into dead protoplasm exhibits a far-reaching resemblance to the transition of a labile substance into an isomeric stable form of atomic migration.

2. Compounds that easily enter into reaction with aldehyds are poisonous for all kinds of organisms. Such compounds have no action upon dead protoplasm or upon common proteids.

3. Compounds that easily enter into reaction with labile amido-groups are poisonous for all kinds of organisms, but these compounds have an action upon ordinary proteids also, and therefore also upon dead protoplasm.

4. There exists widespread in the vegetable kingdom a highly labile proteid serving as reserve material, which undergoes chemical change by the same influences as those which cause the death of the cells.

We are not prepared to say that Dr. Loew's speculations are as yet included among chemical orthodoxies, but they certainly merit a close and candid scrutiny.

The Chemical Analysis of Iron. A Complete Account of all the best known Methods for the Analysis of Iron, Steel, Pig-iron, Iron Ore, Limestone, Slag, Clay Sand, Coal, Coke, and Furnace and Producer Gases. By ANDREW ALEXANDER BLAIR, Graduate United States Naval Academy, 1866; Chief Chemist United States Board appointed to test Iron, Steel, and other Metals, 1873; Chief Chemist United States Geological Survey and Tenth Census, 1880; Member American Philosophical Society, &c. Third Edition. Philadelphia: J. B. Lippincott Company. London: 10, Henrietta Street, Covent Garden.

THE vast extent and growing prosperity of the iron manufacture in the United States have naturally drawn the attention of chemists to metallurgy, and especially the metallurgy of iron. The present work is the natural result of these circumstances, and has most admirably met the demand thus created. The author sets out with instructions for the preparation of samples and an account of the apparatus particularly required in the siderurgical laboratory.

It will be noticed that for crucibles pure platinum is recommended in preference to the iridium alloy, which is "much more likely to crack." Mr. Blair recommends the laboratory to be provided with two balances, one for weighing crucibles, &c., and another, much smaller, for weighing out the portion taken for analysis. Then follow the reagents required, with special instructions for preparing magnesia mixture and molybdate solution. We are glad to observe that the former mixture is directed to be prepared from magnesium and ammonium chlorides without any sulphates.

We then come to the analysis of pig-iron, wrought iron, and steel, involving the determination of sulphur, silicon, slag, and oxides, phosphorus (especially in presence of titanium), manganese, carbon (total, graphitic and combined), copper, nickel and cobalt, chromium and aluminium, arsenic, antimony, tin, tungsten, vanadium, and nitrogen.

Then follow procedures for the analysis of iron ores, of limestones, clay, slags, fire-sands, coal, and coke. Next we come to the analysis of the gases, carbonic acid, carbon monoxide, oxygen and hydrogen, and hydrocarbon CH₄. Then come certain tables.

For calculating the weight of the substance sought for from that of the substance found, we do not meet here or in any other text-book an arrangement as simple as that to be found in Rose, vol. ii., A. Normandy's version (Tegg and Co., 1849).

Blair's work will be found most valuable by all chemists connected with the iron trade.

Catalogue of Case School of Applied Science, Cleveland, Ohio. 1895-96. Cleveland: J. B. Savage.

THIS pamphlet is of no small interest, as it affords us the opportunity of comparing two very distinct systems of higher education; to wit, that prevailing in the United States, and that almost universally established on the European continent. In Europe, Britain always

excepted, all colleges and universities are under the direct and close superintendence of the State. In America, on the contrary, free scope is given to private enterprise. Universities, colleges, schools of science—such as the one described in the publication before us,—may be founded and endowed by any private individual, syndicate, or religious denomination, and may obtain legal incorporation and the power to grant degrees which are officially recognised. The position corresponding to the *Senatus Academicus* is held by a body of trustees. The "courses," or, as they would be called in Germany, "faculties" are in the Case School civil engineering, mechanical engineering, electrical engineering, mining engineering, physics, chemistry, architecture, and general science. The degrees which may be awarded are those of "Bachelor of Science" and "Master of Science." These degrees cannot be obtained without the production of a thesis showing actual work in one or other department. The expense of the course is stated to be from 275 to 350 dollars for tuition, board, room, books, &c., per annum. Among the subjects taught we notice "economics," "civics," and rhetoric, three subjects of little value to the men of science, but priceless to the politician and the agitator. It seems to us that upon some, at least, of the professors is thrown a mass of incongruous work. Thus, Professor Comstock undertakes rhetoric, English, composition, descriptive geometry, biology, in the departments of zoology and botany and geology. If he can teach all these subjects *con amore* he must be something more than an admirable Crichton. The work must be the harder because the botany, zoology, and geology are to be taught not merely from books but in the laboratory. What are the "recitations" mentioned as taking up much of the morning hours? We hope not committing text-book to memory. We are watching the career of the American science schools with the more interest as some of them are now producing good work.

A New Course of Experimental Chemistry, Including the Principles of Qualitative and Quantitative Analysis; Being a Systematic Series of Experiments and Problems for the Laboratory and Class Room. By JOHN CASTELL-EVANS, F.I.C., Senior Demonstrator and Lecturer on Chemistry at the City and Guilds of London Institute's Technical College, Finsbury. London: Thomas Murby, Pp. 244.

WE have been able on a former occasion to congratulate Prof. Castell-Evans on his method of teaching chemistry. He does not lay before his pupils the facts and laws of the science to be read over or "memorised." But he guides them into ascertaining such facts and principles for themselves by a well selected course of experiments. For the performance of these experiments he gives excellent advice. The student who has worked through the problems here laid down in a conscientious and intelligent manner will be worth calling a chemist. Whether he will be able to "pass exams." we do not presume to foretell, but he will certainly be able to take up unsolved questions, theoretical or practical, and to throw a new light upon them.

We much regret, however, to find the author advocating needless complication as regards the denominations of the metric system of weights and measures. We all know that French chemists express the cubic centimetre in the singular or plural number by the abridgement *c.c.*, and that we in this country do the same.

Such abbreviations are perhaps too simple for the Teutonic mind, and we accordingly find German authors, with the signal exception of Prof. Fresenius, writing *c.c.m.* or *c.c.m.s.* Mr. Castell Evans appears to follow their example. Yet he retains the sensible abridgement *m.m.* for millimetre.

In all other respects, as far as we have been able to

trace, the author's precepts and example are alike worthy of being followed.

The "Introductory Remarks" are a perfect mine of precious truth. Thus we read "on no account is he (the student) to be permitted to perform mental gymnastics or conjure with symbols and formulæ." The author speaks of the prospect of chemistry being "raised to the dignity of a deductive science." Such a "rise" would in some senses be small benefit.

Upon the whole Mr. Castell-Evans' method of teaching deserves very general adoption.

Chemical Lecture Experiments.—Non-Metallic Elements. By G. S. NEWTH, F.I.C., F.C.S., Chemical Lecture Demonstrator at the Royal College of Science, South Kensington, London, New York, and Bombay: Longmans, Green, and Co. New and Enlarged Edition, Pp. 344, Crown 8vo. 1896.

THE author's object has been to supply lecturers and teachers with a store of experiments illustrative of the preparation and the properties of the non-metallic elements. The instructions given are full and clear, none of them having been introduced at hearsay, or copied from other books or documents. The author has omitted all dangerous experiments.

Though using the metrical system of measurement, he has given the English equivalents of the French measures of length, justly remarking that, though the British scientific mind has acquired the habit of thinking in grms. and c.c., it still conceives of measures of length in inches. Sources of danger are pointed out where they may occur.

The illustrations are not only numerous and to the purpose, but very correctly and clearly drawn.

Not merely the teacher but the student will find this work very useful, as it will often save him the trouble of sketching the apparatus which he sees in use on the lecture table. Hence Mr. Newth's work will prove a valuable companion to any text-book of the chemistry of the non-metallic elements and their compounds.

University College of North Wales, Calendar for the Year 1896-7. Manchester: J. E. Cornish.

WE have here a full prospectus of the North Wales University College, and are glad to recognise what are, in our opinion, steps in the right direction. Thus, if we do not misunderstand this calendar it will be open practically for a student to proceed to the degree *Baccalaureus in Scientia* without any course of study in classics. The "departments" of studies seem essentially to correspond to the distinct faculties in the Continental Universities. Chemistry, physics, and biology seem to receive an approximately fair share of attention, and special laboratories are devoted for their study. There are rooms for photography, for gas analysis and for spectroscopic work, a physical and a chemical lecture theatre, a chemical museum, an optical room, a room for electrical measurements, biological laboratories and lecture theatres (botanical and zoological). A very important feature is the agricultural department. In short, as far as we can judge from a careful examination of the descriptions and plans of the laboratories, there is here scope for genuine work in the sciences concerned.

A fact showing that the authorities of the College really "mean business" is that the chemical and physical departments were opened in February, 1885, by Lord Kelvin, with an appropriate address. We trust that the College will make good use of the facilities placed at its disposal.

Should there not be a special mining and metallurgical department?

CORRESPONDENCE.

ACTION OF THE METALS AND THEIR
SALTS ON THE ORDINARY AND ON THE
RÖNTGEN RAYS.

To the Editor of the Chemical News.

SIR,—In an interesting paper on the above subject, communicated to the British Association in September, by Messrs. Gladstone and Hibbert, and fully reported in the CHEMICAL NEWS (lxiv., 235), reference is made to the first workers in this field, who are specially mentioned by name. The authors omit the names of W. Ackroyd and H. B. Knowles, who, in a joint paper to the Physical Society of London, clearly showed by a photograph submitted to a Meeting on March 13th, and which had been taken on the previous 20th February, that "selective absorption of the X rays is a function of the atomic or molecular weight." These experimenters were the first in England to enunciate the fact, and the results of any foreign work were not as yet to hand.

In the writer's little work on "The Old Light and the New" (Chapman and Hall), published in April, the law is shown to hold for the elements in the periodic groups I., II., IV., V., and VIII. See pp. 73–80 in a copy forwarded.—I am, &c.,

WM. ACKROYD.

ESTIMATION OF SULPHUR IN CAST-IRON
OR STEEL.

To the Editor of the Chemical News.

SIR,—As regards the method described by G. G. Boucher (CHEMICAL NEWS, lxiv., p. 74) I would point out that it is not new; as, in the *Journal of the Iron and Steel Institute* (1888, Part II.) there appears an abstract of an article, by C. Meincke, in which practically the same method is given for the determination of sulphur in pig-iron and spiegeleisen.—I am, &c.,

J. JAS. MORGAN.

10, Bryntirion Street, Dowlais.
Nov. 13, 1896.

Society of Arts.—The first course of Cantor Lectures at the Society of Arts will be by Professor Vivian B. Lewes, on "The Use of Gas for Domestic Lighting." The subjects dealt with include:—The principles of illumination and the measurement of light; flat flame, Argand, and regenerative burners; incandescent mantles and burners; the effect of globes in diffusing and absorbing light; atmospheric influences and the penetration of light; gaseous illumination where coal-gas is not available; oil-gas and its properties; acetylene, its manufacture and use. The course commences on Monday, the 23rd inst., and will be continued on the two following Mondays.

Determination of Volume of Pulverulent Bodies by Shaking.—Gluckmann (*Pharm. Central Halle*).—A cylindrical measure, 20 c.m. in height and 2½ c.m. in diameter, graduated in c.c. from its flat bottom upwards, is charged with the powder in question and then knocked upon a support (not too hard) until there occurs no further decrease in volume. If the volume is then divided by the weight of the quantity of substance used we obtain a value which the author names relative volume.

CHEMICAL NOTICES FROM FOREIGN
SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Analytische Chemie.
Vol. xxxv., Parts 4 and 5.

The Chemical Examination of Cheese.—A. Stutzer. —The author determines the ash and its constituents, employing a platinum capsule in a muffle furnace. For the other determinations a considerable quantity of the cheese is well rubbed up with quartz sand, previously washed, ignited, and sifted, the proportion taken being 100 grms. cheese to 400 grms. of sand. The total nitrogen is estimated by the Kjeldahl method. Cupric hydroxide is an unsuitable precipitant for the albumenoids if they are mixed with pancreas-peptone. The author uses phosphotungstic acid for separating the valuable caseins and albuminates, and their first scission products (including the albumoses and pancreas-peptones), from the worthless decomposition products, such as phenylamido, propionic acid, tyrosin, leucin, and other amides. IV. The nitrogen present in the state of ammoniacal salts is estimated by distillation with barium carbonate. V. Nitrogen in the state of amides is found as the nitrogen of compounds not perceptible by phosphotungstic acid and not belonging to ammonia. VI. The indigestible nitrogenous matter is found as the residue not acted on by rennet. VII. The determination of nitrogen existing as albumose and peptones. VIII. The caseins and albuminates are found by deducting from the total nitrogen the nitrogen not precipitable by phosphotungstic acid (V.), the indigestible nitrogen (VI.), and the nitrogen existing as albumose and peptone (VII.).

The Examination of Commercial Thorium Nitrates and the Separation of Ceria and Thoria.—R. Fresenius and E. Hintz.—This paper will be inserted in full.

Prevention of Corrosive Liquids being Drawn into the Mouth when filling Pipettes.—F. F. Skinner (CHEMICAL NEWS).

Regulating Cock for adjusting Temperature in Distillation, Desiccation, &c.—G. Hansdorff (*Zeit. f. Angewandte Chemie*).—On the plug of the glass cock is fixed a one-armed lever with a circular scale.

Iron Wire Nets with Asbestos Covers.—Sohnie-windt (*Zeit. Ange. Chemie*).—The author pronounces such nets little inferior to metal gauze.

A Modification of the Litre Flask.—W. M. B. Giles (CHEMICAL NEWS).

An Analytical Funnel.—R. Muencke.—Shown in an accompanying figure.

A Celluloid Funnel.—A. H. Edwards (CHEMICAL NEWS).

Gas-generators, especially for Sulphuretted Hydrogen.—J. F. Liversidge.—From the CHEMICAL NEWS.

Bunsen Burner, with a Safety-basket of Wiresetting.—(Joint-Stock Co. for water-leads and installations for lighting and heating).—On the principle of the Davy safety-lamp.

Substitute for the Chemical Balance.—H. Joshua Phillips (CHEM. NEWS).

Modification of the Nitrometer.—Emile Henry (*Bull. de la Soc. Chim. de Paris*).

Apparatus for Drying and Absorbing Gases in Elementary Analysis.—James Leicester.—From the CHEMICAL NEWS.

Refrigerator for Distillations from a Test-glass.—C. J. Brooks.—From the CHEMICAL NEWS.

Hot-water Funnel.—C. R. Beck (CHEMICAL NEWS).

Volatilisation of Salts during the Evaporation of Water.—G. H. Bailey.—From the *Journal of the Chemical Society*.

Expansion of Water on Change of Temperature.—Stephane de Lannoy.—From *Comptes Rendus*, cxx., 866.

New Method of Quantitative Spectral Analysis.—G. and H. Krüss.

Direct Spectroscopic Examination of Minerals and of some Fused Salts.—A. de Gramont.—From *Comptes Rendus*, cxxi., p. 121.

Separation of three Liquids by Fractionated Distillation.—F. R. Barrell, G. L. Thomas, and Sydney Young.—From the *CHEMICAL NEWS*.

Measurement of High Temperatures, especially of the Melting-points of some Inorganic Salts.—John McCrae (*Annalen der Physik und Chemie*).—Already noticed.

Determination of Fusion and Ignition Points.—W. R. Hodgkinson.—From the *CHEMICAL NEWS*.

Heating by Electricity.—L. C. Levoir.—From the *CHEMICAL NEWS*.

Loosening Glass Stoppers.—R. W. Hill.—From the *CHEMICAL NEWS*.

Cleansing Port-Objects from Oil, Canada Balsam, &c.—Zettnow (*Central Blatt für Bakteriologie*).—The author steeps covering-glasses in oil of turpentine, then boils in hydrochloric acid and potassium chlorate. Finally the glasses are heated in a paste of powdered steatite, sawdust, soda, and water, rinsed in hot water, in water containing hydrochloric and acetic acids, and finally rinsed with alcohol.

Normal Barometer for the Laboratory.—K. R. Koch (*Annalen der Physik und Chemie*).—A syphon barometer with an upper and lower expansion, into each of which is fused a thermometer graduated into tenths of a degree. In connection with the barometer is a distillatory globe from which fresh mercury can be distilled into the apparatus. A Crookes tube is also connected with the apparatus to test the vacuum.

A Consistency Meter.—Weiss.—A patented device, which cannot well be described without the aid of illustrations.

Construction of the Slit of Spectroscopes.—W. Crookes.—From the *CHEMICAL NEWS*.

A Dephlegmator.—Sydney Young and E. L. Thomas.—From the *CHEMICAL NEWS*.

Taking Samples of Water for Bacteriological Purposes.—W. T. Burgess.—From the *CHEMICAL NEWS*.

Extraction Apparatus.—L. L. de Koninck (*Chemiker Zeitung*).—This paper requires the accompanying figures.

Apparatus for Extracting Soluble Phosphoric Acid from Superphosphates.—W. D. Horne.—From the *CHEMICAL NEWS*.

Revolver Pipette.—A. Stutzer (*Zeit. Angew. Chemie*).—The lower end is provided with a two-way cock.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Society of Arts, 8. "The Use of Gas for Domestic Purposes" (Cantor Lectures), by Prof. Vivian B. Lewes.

WEDNESDAY, 25th.—Society of Arts, 8. "Recent Developments in Mechanical Road Carriages," by J. Worby Beaumont, M.Inst.C.E.

FRIDAY, 27th.—Physical Society, 5. "Apparatus for giving Diagrams of the Efficiency of a Photographic Shutter," by Captain Abney, F.R.S.

TO CORRESPONDENTS.

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1931.

THE ALLEGED NEW ELEMENT, LUCIUM.

By WILLIAM CROOKES, F.R.S.

THROUGH the kindness of M. P. Barrière, the patentee of Lucium, I have been placed in possession of a solution of lucium nitrate, and a larger quantity of precipitated oxalate, both said to be tolerably pure. I have thus been enabled to try a sufficient number of experiments to convince me that the claim of lucium to form one of the chemical elements is not justified.

Preliminary examination with a hand spectroscope showed the presence of didymium and erbium in small quantities. The nitrate solution was evaporated to dryness and ignited. It left a cream-coloured earth, easily soluble in dilute nitric acid. The oxalate on ignition gave an earth having similar properties.

Radiant matter tests were made of the original earth. It phosphoresced very well when submitted to the induction current in a vacuum tube, and the spectrum of the emitted light was that of yttria. All the lines and bands were there, but they were deficient in sharpness, showing the presence of impurities.

A larger quantity of oxalate was converted into nitrate and evaporated to dryness and submitted to fractionation by partial decomposition by fusion. Five operations in all were performed, and similar radiant matter tests were performed on the two extremes and on the centre earth. All showed the yttrium phosphorescent spectrum. The fusing nitrates required a high temperature for decomposition, like yttrium nitrate; the extremity at the + end was in consequence larger than that at the - end. On the + side the didymium bands in the absorption spectrum gained in intensity, while on the - side they were very faint.

Portions of the earths from each fraction were converted into sulphates, ignited, and tested in the radiant matter tube. The result showed that the removal of the more easily decomposable nitrates from the fraction at the + end brought out the sharpness and brightness of the yttria bands, this fraction phosphorescing almost like pure yttria. A similar radiant matter test on the extreme fraction at the - end gave a poor yttria spectrum, the erbium phosphorescent spectrum being also visible.

Photographs were taken of the ultra-violet spectrum of lucium. The spectrograph has a complete quartz train, and the pictures were taken on films curved to the proper curvature to get all the lines in focus at once. The nitrate in strong solution was put into an appropriate tube, and sparks from a large induction coil, having a jar intercalated, were passed between the solution and a platinum pole; a very short spark being employed. The lines in the lucium spectrum closely resemble those in the yttrium spectrum. Spectra were taken of lucium and yttrium, partially superposed so as to detect close coincidences, and on examining several hundreds of lines only six in the lucium spectrum were seen to have no counterpart in the yttrium spectrum. To make certain that I was working with pure yttrium, I used three specimens of the earth and with each I took superposed spectra of lucium: yttria prepared by Clève, called by him "purissimum"; yttria prepared by Marignac, and called by him quite pure; yttria prepared by myself, as pure as I could make it.

To ascertain the absence or presence of other bodies, I compared the lucium spectrum with spark spectra of the following earths, as pure as I could prepare them:—Yttrium, erbium, ytterbium, scandium, thulium, holmium, thorium, didymium, lanthanum, zirconium, glucium,

aluminium, and calcium. In most cases the spectra of lucium and the earth under comparison were photographed partly superposed on the same plate.

Of the six lines unaccounted for, four of them are extremely faint and belong to platinum or air. The fifth line is also faint and is due to a trace of zirconium. The sixth line is strong, and is coincident with a strong line in the ytterbium spectrum.

Spectrum analysis along two different directions shows, therefore, the so-called lucia to be nothing more than yttria in a rather impure condition.

By the kindness of M. Schützenberger, I have received details of the chemical operations through which the monazite passed to separate the lucia from it. They do not materially differ from those given in the patent reprinted in the CHEMICAL NEWS.* The material part of the preparation is the use of sodium thiosulphate, which is said to precipitate lucium and not yttrium. Knowing from long experience the incompleteness of this reagent in separating bodies, I tried the following experiments:—

1. A solution of pure neutral nitrate of yttrium was mixed with a concentrated solution of thiosulphate of sodium, and the action started by heat. As soon as the boiling-point was reached, a slight precipitate was formed, and the liquid was allowed to cool. (In this operation I followed strictly the directions in the patent for separating lucium from yttrium—the lucium precipitating and the yttrium remaining in solution). The precipitate was filtered off and the solution precipitated with ammonia. It was by far the larger quantity of the two.

The small quantity of earth precipitated by sodium thiosulphate was tested in a radiant matter tube and gave the phosphorescent spectrum of yttria. The earth precipitated from the thiosulphate solution was likewise tested in a radiant matter tube and gave also the phosphorescent spectrum of yttria.

Spark spectra were photographed from each of these earths, with the result that they equally showed the lines belonging to yttrium, with no admixture of other lines.

2. Some nitrate of lucium, prepared from M. Barrière's oxalate of lucium, was put through exactly the same treatment to which I submitted the pure yttria in Expt. 1. As in the former case, sodium thiosulphate split it into two portions, the smaller being precipitated and the larger remaining in solution. These two portions were then tested in the radiant matter tube and with the spark, with the result that they each gave an yttria spectrum.

3. A mineral closely allied to monazite, containing a mixture of rare earths, was treated according to M. Barrière's patent, and a small quantity of an earth was obtained which had been separated from the bulk of the yttria present by precipitation with sodium thiosulphate. This was tested by the two spectrum methods and was found to be yttria.

Chemical examination, therefore, confirms the results obtained by spectrum observations, that lucium is nothing but impure yttrium. The error has arisen by considering the sodium thiosulphate separation as a complete one; whereas yttria partially comes down if the solutions are strong and heated.

Too much weight is attached to the fact of the atomic weight of lucium being 104, that of yttrium being 89. The following are the usually accepted atomic weights of the associated earths which may possibly be present:—

Scandium	44.5
Yttrium	89.0
Didymium	142.0
Samarium	250.0
Erbium	166.0
Ytterbium	173.0
Thorium	233.6

Considering that didymium and erbium can be detected in the lucium sent me by their absorption bands, and

* No. 1927, October 30th, 1896.

that ytterbium is shown to be present by a strong line in the spark spectrum, it is not surprising that the presence of bodies of such high atomic weights should raise the atomic weight from 89 to 104.

ARGON AND HELIUM.

By Lord RAYLEIGH, F.R.S.

IN his discussion of the probable character of argon and helium, Dr. Brauner (CHEMICAL NEWS, vol. lxxiv., p. 223) seems to leave out of account the evidence derived from the refractivities of the gases. The refractivity of argon is certainly less than that of nitrogen, and the refractivity of helium is much less than that of hydrogen (*Proc. Roy. Soc.*, Jan., 1896); so that, according to the view he favours, N_2 is less refractive than N_2 , and H_4 than H_2 . Is this credible?

Dr. Brauner expects important information from determinations of specific heat. Doubtless they will be interesting, but I see no reason to anticipate that the results will differ sensibly from the numbers now available calculated from the laws of thermodynamics. The ratio of the specific heats is already known, and by Mayer's principle their difference is readily expressed (see, for example, "Theory of Sound," § 246). From the ratio and the difference both values follow, and that without any special molecular hypotheses.

November 20, 1896.

EXPLANATION OF THE RÖNTGEN RAYS.

By Dr. T. L. PHIPSON.

FROM all experiments made up to the present time I have come to the following conclusions:—

1. They exist in sunlight, as shown in my note in the CHEMICAL NEWS (vol. lxxiii., p. 223).

2. They exist in the lower part of the spectrum:—

White light { Prism of } Heat rays (ultra-red).
or { organic } Light rays (colour).
sunlight { matter } Electric rays (ultra-violet, actinic, or X rays).

3. They traverse all organic substances, but are more or less arrested by mineral substances, because all the latter contain a metal, and metals being good conductors they run over the metal.

4. They discharge electrified bodies, because they are electric rays and supply the contrary electricity.

5. They act on the photographic plate, as a galvanic current acts on salts, &c.

6. They emanate from various phosphorescent or fluorescent substances.

The Casa Mia Laboratory, Putney,
November 20, 1896.

SUCCESSION OF THE ATOMIC WEIGHTS OF SIMPLE SUBSTANCES.

By M. DELAUNEY.

I HAVE used in this study the tables of atomic weights given by MM. Mendeleeff and Lothar Meyer, and by the "Annuaire du Bureau des Longitudes." For the values of atomic weights of the simple bodies I have taken the whole numbers which approach nearest to the numbers in the tables.

I have divided the atomic weights thus rectified into

four classes, according as they are multiples of 4 or multiples of the same number + 1, 2, or 3.

First Class.—Atomic Weights Multiples of 4.

The atomic weights which are multiples of 4 are contained in the following table:—

12 Carbon	124 Antimony
16 Oxygen	128 "
24 Magnesium	132 Cæsium
28 Silicon	136 "
32 Sulphur	160 Gadolinium
40 Calcium	172 "
44 Scandium	176 Ytterbium
48 Titanium	184 Tungsten
52 Chromium	188 "
56 Iron	192 Iridium
80 Bromine	200 Mercury
92 Cerium	204 Thallium
96 Molybdenum	208 Bismuth
104 Rhodium	212 "
108 Silver	216 "
112 Cadmium	240 Uranium
120 Antimony	

It is to be remarked that the numbers entered in this table are obtained in the same manner in each column by adding successively, setting out from the head of each column, the numbers 4, 8, 4, 4, 8, 4, 4, 4, 4, 24.

The head of the first column being 12, the two others follow from 80 to 80.

The table presents gaps due probably to simple bodies as yet unknown, or to atomic weights badly determined.

Second Class.—Atomic Weights Multiples of 4 + 3.

The atomic weights of the second class appear to follow the same succession as those of the first, but setting out from 7 instead of 12. This table has only two columns.

7 Lithium	87 Strontium
11 Boron	91 "
19 Fluorine	99 "
23 Sodium	103 Ruthenium
27 Aluminium	107 "
35 Chlorine	115 "
39 Potassium	119 "
43 "	123 "
47 "	127 Iodine
51 Vanadium	131 "
75 Arsenic	155 "

We observe that certain bodies whose atomic weights are multiples of 4 + 3 do not figure in this table. These are—Phosphorus (31), manganese (55), cobalt and nickel (59), copper (63), selenium (79), lanthanum (138), thulium (171), osmium (195), lead (207), thorium (231). On the other hand, we find in the table numerous gaps. Now, these latter seem to correspond to elements which, not being able to subsist, have been decomposed each into two others, whose absence we have pointed out. We have, in fact:—

2 × 43 = 31 (P)	+ 55 (Mn)
2 × 47 = 31 (P)	+ 63 (Cu)
2 × 91 = 79 (Se)	+ 103 (Ru)
2 × 99 = 59 (Co or Ni)	+ 139 (La)
2 × 107 = 7 (Li)	+ 207 Pb = 19 (F) + 195 (Os)
2 × 115 = 59 (Co or Ni)	+ 171 (Thul)
2 × 119 = 7 (Li)	+ 231 (Th)

Third Class.—Atomic Weights Multiples of 4 + 2.

The atomic weights of the third class are few in number. They are:—

2 Helium	106 Palladium
14 Nitrogen	126 Tellurium
70 Gallium	182 Tantalum
90 Yttrium or Zirconium	194 Palladium

These atomic weights are obtained by setting out from 2 and adding successively 12, 56, 20, 16, 20, 56, 12; numbers which present a remarkable symmetry.

Fourth Class.—Atomic Weights being Multiples of 4 + 1.

The atomic weights of this class are, again, less numerous than those of the former groups, but they appear to follow an analogous law.

9	Glucinium	101	Rubidium
65	Zinc	121	"
85	Rubidium	177	"

Barium (137), which belongs to the fourth class, seems to be produced by the decomposition of the unstable elementary body 101, as it has been already indicated for the second class. We have, in fact,—

$$2 \times 101 = 65 \text{ (zinc)} + 167 \text{ (barium)}.$$

N.B.—A certain number of simple bodies are not mentioned in any of the four classes above mentioned. There are some bodies as yet little known, such as argon, holmium, neodymium, praseodymium, and terbium; then such bodies as didymium, iridium, and niobium, the atomic weights of which are not established; and, lastly, tin and gold. For tin we hesitate between 117.35 and 118, and for gold between 196.2, 196.6, and 199.

A better knowledge of the atomic weights of the above bodies seems as if it should cause these exceptions to disappear.—*Comptes Rendus*, cxxiii., p. 600.

PROXIMATE CONSTITUENTS OF COAL.*

ACCORDING to Baltzer (*Vierteljahrsschr. d. Zür. Naturf. Gesellsch.*, 1872; also Muck, *Chem. d. Steink.*, p. 141) coals are mixtures of complex carbon compounds, these forming a genetic and possibly a homologous series. The framework of carbon contained in these compounds is a complex one, the only analogy to which is that presented by the aromatic compounds. The physical properties of coals are such as to render a classification possible, and these different varieties exhibit a similarity in their ultimate composition. Whilst these several varieties form the essential constituents of coal, there are in addition certain accessory constituents, such as the resinous components, the hygroscopic water, and the "enclosed gases."

The researches of J. W. Thomas, of E. von Meyer, of Schondorff, of Bedson and McConnell, and others, have provided an extensive knowledge of the nature of the gases enclosed in coals from different sources, and also a knowledge of the conditions under which these gases are retained by the coal. The hygroscopic water and the absorptive power for water of different coals have, by reason of their technical importance, received considerable attention.

The remaining group of accessory constituents represented by the resinous bodies, which are distinguished from the coal substance by their solubility, consists of some few hydrocarbons, such as ozokerit, and bodies containing carbon, hydrogen, and oxygen, of which Muck, in his "*Chemie der Steinkohle*," gives the following:—i. Middletonite; ii. Pyroretinite; iii. Reussinite; iv. Scleretinite; v. Rosthornite; vi. Anthrakoxen; vii. Guayaquilite; viii. Berengelite.

These mineral substances are of varying solubilities in alcohol, ether, and turpentine. From the description given by the different investigators it would appear probable that several of these substances are mixtures.

* Report of the Committee, consisting of Sir I. Lowthian Bell (Chairman), Professor P. Phillips Bedson (Secretary), Professor F. Clowes, Dr. Ludwig Mond, Professor Vivian B. Lewes, Professor E. Hull, Mr. J. W. Thomas, and Mr. H. Bauerman. Read before the British Association (Section B), Liverpool Meeting, 1896.

In 1874 Dondorff drew attention to the occurrence in several Westphalian gas coals of a blackish solid, with a reddish brown colour in reflected light, having a brown streak. This substance is found in thin leaflets on this coal, and is almost entirely soluble in ether, forming a light yellow solution, which fluoresces not unlike solutions of the salts of quinine.

By the extraction of a Westphalian gas coal with ether, Muck has obtained an ethereal solution of a similar character, and from it obtained a solid of the following percentage composition:—

C=87.22, H=9.20, O=2.29, S=1.29 (nitrogen absent).

This substance, when heated in a platinum crucible, leaves a coke-like residue amounting to 32.09 per cent. The author considers this substance to be widely diffused in coal, and has shown it to exist in varying amounts in different parts of the same seam. Associated with this investigation is that of P. Siepmann, who has submitted the gas coal of the Pluto mine, Westphalia, to a systematic extraction with chloroform, ether, and alcohol, obtaining the following results:—

The chloroform extract amounted to 1.25 per cent of the coal; the solution, dark yellow to brown in colour, possessed a strong green fluorescence; the composition of the extract was—

C=83.46, H=7.93, O=4.27, N=2.71, S=1.63.

The residue, after extraction with chloroform, gave, when treated with ether, a light yellow solution, having a bluish green fluorescence, from which a solid was obtained amounting to 0.3 per cent of the coal, and containing—

C=84.82, H=10.51, and O=4.67.

The residue, treated with alcohol, gave a solution similar in character to the ethereal solution. The amount removed by the alcohol was 0.25 per cent of the coal, and the composition of the dissolved solid was found to be—

C=72.52, H=10.08, O=17.4.

After the above treatment the residual coal was again extracted with chloroform, which removed 0.75 per cent of the coal, and left on evaporation a dark brown, pitch-like mass, which gave the following results on analysis:—

C=78.82, H=8.56, O=9.97, N (trace), S=2.65.

The last chloroform solution was dark brown in colour and feebly fluorescent.

The composition of the coal before and after this treatment is given below:—

	C.	H.	O.	N.
Before treatment..	80.31	5.50	12.94	1.25
After treatment ..	74.00	4.77	20.09	1.14

According to H. Reinsch, alcohol extracts from coal a substance supposed to be altered "chenopodin," a body which the author had discovered in the sap of *Melilotus albus*, and to which he attributes the composition $C_{12}H_{13}O_8N$. In 1885 P. Reinsch concluded that coal consists of two classes of substances, one soluble in alkalis, forming coloured solutions, and a second insoluble.

By the use of phenol as a solvent E. Guignet has extracted from 2 to 4 per cent of a brown solid from coal, which is precipitated from the solution by alcohol. The finely-powdered coal, treated with nitric acid, yields solutions containing oxalic acid and trinitroresorcinol; the insoluble residue contains apparently nitro-compounds, or bodies similar to nitro-cellulose. A portion of this residue is dissolved by caustic alkalis and ammonia, forming brown-coloured solutions.

Guignet, led by the formation of trinitroresorcinol, as mentioned above, attempted to obtain resorcinol by fusion of the coal with caustic soda and distillation in a bath of molten lead, but obtained ammonia and aniline only. The residue after this treatment was, however,

found to be partially dissolved by water, forming dark brown solutions, from which acids precipitated out humus-like substances. Guignet concludes these bodies are derived from the cellulose residues of the coal, and that the trinitroresorcinol owes its origin to the resinous and wax-like constituents.

During the Session 1889-90 Mr. Saville Shaw, Lecturer in Chemistry at the Durham College of Science, Newcastle-upon-Tyne, made some experiments on the action of a mixture of concentrated sulphuric and nitric acids on bituminous coal. The coal, in a finely-powdered condition, was allowed to remain for three weeks in contact with the mixed acids, and then poured into a large volume of water, filtered, and thoroughly washed. The dried residue differs but slightly in appearance from the original coal, but had evidently undergone change in composition, as after this treatment it gave as much as 77 per cent of "volatile matter," whereas the coal contained but 27 per cent; further, when heated in a test-tube it "puffs" with slight flame, resembling in this respect gun-cotton. A considerable proportion of this "nitro-coal" is soluble in caustic alkalies, yielding very dark brown solutions, from which on acidifying bulky dark brown precipitates are formed. The precipitates, washed and dried, form brilliantly black friable masses, which have not the semi-explosive properties of the original "nitro-coal." Methyl alcohol dissolves some 11 per cent of the nitro-coal, the solution yielding a black scaly product on evaporation, which when heated suddenly decomposes, leaving a very bulky residue of carbon. Attempts to prepare reduction products from this "nitro-coal" were unsuccessful.

In a note published in the *Proceedings of the Chemical Society* (1891-92, p. 9), R. J. Friswell described results obtained by treating finely-powdered coal with dilute nitric acid; a considerable portion of the coal is thus converted into a black insoluble acid, which behaves very much like a "nitro-compound."

Mention should also be made of the investigations of Mr. Watson Smith, published in 1891, on the soluble and resinoid constituents of bituminous coal. The soluble material extracted by benzene from a Japanese coal Mr. Watson Smith has shown to contain phenols, nitrogenous organic bases, and also some aromatic hydrocarbons.

In a previous report experiments with various solvents on a bituminous coal, from the Hutton seam in the county of Durham, were referred to, but, owing to the small yields obtained, this method of attacking the problem as to the nature of the proximate constituents of coal has been relinquished.

The oxidation of the finely-powdered coal with aqueous solutions of potassium permanganate, in some cases made alkaline with caustic potash, appeared to offer a more promising method of attack. The coal uses up very considerable quantities of the permanganate, and dark brown solutions are obtained. From these solutions it has been attempted, by the aid of the formation of insoluble salts, to isolate some of the acids which result from the oxidation of the coal in this way. The difficulties met with arising from the unsatisfactory properties of many of these salts, which are usually obtained in the form of gelatinous, clayey solids, difficult to wash and to obtain in a state of purity suitable for analysis, have led to the abandonment of this reagent.

More promising results have been obtained by adding upon the coal with dilute hydrochloric acid and potassium chlorate. Mr. J. A. Smythe, B.Sc. of the Durham College of Science, Newcastle-upon-Tyne, has undertaken the investigation of this action for the purposes of this Committee.

When finely-divided coal is boiled for several hours with dilute hydrochloric acid, and potassium chlorate added from time to time, the coal gradually assumes a brown colour, and a brown acid collects on the surface of the yellow liquid. The coal, after lengthened treatment, is filtered off, washed, and dried at 100° C. The product

is invariably found to have increased in weight, and when extracted with alcohol or acetone some 30 to 35 per cent of the material is dissolved out by either of these solvents; of the two, acetone is the more powerful solvent, leaving a coal-like insoluble residue. The solution obtained in this manner is next distilled, and after removal of the solvent a dark reddish brown resinous mass is left, which, when finely ground, forms a dark brown homogeneous powder. The finely-divided powder was extracted with benzene; the portion insoluble in benzene was treated with alcohol in which some readily dissolved, leaving a residue sparingly soluble in hot alcohol.

(To be continued).

SOURCES OF ERROR IN VOLHARD'S AND SIMILAR METHODS OF DETERMINING MANGANESE IN STEEL.*

By GEORGE AUCHY.

(Concluded from p. 249).

Volhard's Method (continued).

TAUGHT suspicion by the experience thus far had, it was resolved to test every step in the method; and the following determinations were made to see if the temperature of the liquid at the time of neutralisation with zinc oxide had any influence upon the result:—

TABLE VIII.

Solution heated to boiling with the zinc oxide.			Zinc oxide to cold solution.		
No.	Manganese taken. Per cent.	Manganese found. Per cent.	No.	Manganese taken. Per cent.	Manganese found. Per cent.
1	0.40	0.49	1	0.40	0.40
2	0.40	0.44	2	0.40	0.40
3	0.40	0.43	3	0.40	0.40
4	0.40	0.47	4	0.40	0.40
5	0.40	0.42	5	0.40	0.40
6	0.40	0.41	6	0.40	0.39
Solution merely warm.			7	0.40	0.40
1	1.20	1.22	8	0.40	0.41
2	0.80	0.83	9	0.40	0.40
			10	0.80	0.80
			11	1.20	1.20

These results show that neutralisation must be performed in the cold. The writer had always practised this precaution, though for no well-defined reason.

The second series of results in the table also show that there is no tendency to slightly high results, as is the case when titration is done in nitric acid solution (Stone's method).

Volhard, in his article, states that the precipitated manganese dioxide is mixed with protoxide unless some metallic base like zinc oxide, lime, magnesia, &c., be present; and, therefore, in the following experiments on this point it was expected that the results would be poor, since the amount of zinc oxide present was purposely kept as low as possible by making the neutralisation first with sodium carbonate, and then cautiously adding sulphuric acid till slightly acid, the slight excess of acid being then neutralised with zinc oxide.

TABLE IX.

No.	Taken. Per cent.	Found. Per cent.	No.	Taken. Per cent.	Found. Per cent.
1	0.40	0.41	4	0.40	0.41
2	0.40	0.42	5	0.40	0.42
3	0.40	0.40			

* *Journal of the American Chemical Society*, xviii., No. 6, p. 498.

These results seem to show that this is not a very important source of error. In Särnström's method the point is entirely disregarded.

Five determinations made with 5 c.c. free sulphuric acid (2 to 1) at time of neutralisation with zinc oxide give, instead of the theoretical 0.40 per cent taken, respectively 0.40 per cent, 0.42 per cent, 0.41 per cent, 0.41 per cent, 0.41 per cent.

With 6 c.c. free acid, 0.40 per cent, 0.41 per cent.

With 8 c.c. free acid, the results of Table VIII.

Särnström's Method.

Messrs. Mixer and Du Bois recommend this method for iron ores (*Fourn. Am. Chem. Soc.*, xviii., 385), and give results showing its accuracy. In this method zinc oxide is not used, the neutralisation (hydrochloric acid solution) being effected entirely by sodium carbonate, with care not to add it in greater amount than necessary to precipitate the iron, and the subsequent titration is done without filtering off the ferric oxide thus precipitated. This manner of neutralisation leaves the solution not thoroughly neutralised, and from the foregoing results of this article we should expect high results from Särnström's method. The results given by Messrs. Mixer and Du Bois are, however, excellent results; and this indicates either that neutralisation with sodium carbonate in hot hydrochloric acid solution is not attended with the same phenomena as neutralisation with zinc oxide in nitric and sulphuric solutions, or that in the former process there is a greater tendency of the manganese to precipitate with the iron, and that the error from this source counterbalances the error from titrating in faintly acid and hot solution. But the uniform excellence of the results given by Messrs. Mixer and Du Bois points to the former as the more likely supposition. The method was briefly tested by taking standard manganese solution. Instead of 0.40 per cent manganese taken in one case, 0.44 per cent, and in another 0.38 per cent was obtained. But the test was not a fair one, as there was no iron present to give the exact point of neutralisation as obtained in the regular working of this method. Ferric chloride should have been added, but none was at hand, and the writer postponed further examination of the method for the reason that (as explained by Messrs. Mixer and Du Bois) it is not well adapted to the analysis of steel.

Colour Method.

The colour method has no kinship to Volhard's, and its consideration is therefore hardly relevant here. But, nevertheless, as it was found necessary in the course of this work to make determinations by this method for comparison with others obtained by Volhard's method in samples almost used up, it might perhaps be just as well to give these colour results in detail, as showing the limits of error in the process when performed by one not an expert in its use.

The results in the table by Volhard's and by Stone's method were obtained by an observance of precautions given—correction of 0.02 per cent in results by the latter method, thorough neutralisation by zinc oxide, &c.

It will be seen that colour method results are quite accurate if a number of colour comparisons be made and the average taken. But if only one test be made the variation may occasionally be 0.02 to 0.03 per cent. But in these determinations the boiling was all done over the naked flame. Closer results can perhaps be had by using the calcium chloride bath for this purpose, as directed in Blair's "Chemical Analysis of Iron."

Recapitulation.

The sources of error, then, in Volhard's process, as indicated by the foregoing experiments, are:—

1. The incomplete neutralisation by zinc oxide, giving usually high results.
2. The too sudden addition of the necessary excess of zinc oxide, giving frequently low results.

TABLE X.

No.	First reading.	Second reading at		Volhard or gravi-
	Per cent.	a higher dilution.	Per cent.	metric method.
			Per cent.	Per cent.
289	0.40 0.395 0.40 0.63	0.40 0.39 — 0.64	0.40	0.40 Volhard.
153	0.61 0.639 0.552 0.564	— 0.65 0.547 0.560	0.64	0.64 Volhard.
503	0.572 0.543 0.43 0.426	0.586 0.555 — 0.416	0.56	0.56 Stone.
503	0.42 0.42 0.495 0.49	0.425 0.42 0.49 0.48	0.423	0.41 Volhard.
505	0.485 0.495 0.44 0.425	0.485 0.495 0.425 0.425	0.49	0.49 Stone.
483	0.53 0.54 0.38 0.39	0.534 0.546 0.37 —	0.54	0.38 Stone.
471	0.48 0.48 0.438 0.47	0.48 0.486 0.445 0.466	0.48	0.46 Volhard.
490	0.468 0.43 0.43 0.488	0.47 — 0.44 0.472	0.46	0.42 Stone.
493	0.497 0.49 0.50 0.455	0.498 0.475 0.49 0.454	0.49	0.485 Gravimetric.
481	0.47 0.446 0.476 0.43	0.46 0.446 0.47 0.426	0.469	0.455 Gravimetric.
453	0.416 0.449 0.427 0.427	0.425 0.446 — 0.42	0.425	0.425 Stone.
456	0.416 0.417 0.545 0.53	0.428 0.414 0.56 0.53	0.43	0.41 Gravimetric.
451	0.54 0.52 0.52 0.537	0.54 0.52 0.525 0.545	0.53	0.52 Gravimetric.
	0.535	0.531		

3. The titration in nitric acid solution giving results 0.01 or 0.02 per cent too high.

4. Neutralisation by zinc oxide in hot solution, giving high results.

With regard to the first of these sources of error it may be remarked that Volhard recommends slightly acidifying with nitric acid before titration—to oxidise organic matter. But whatever organic matter may be present capable of being oxidised by nitric acid has already been oxidised, and the organic matter and proto salts present in the sodium carbonate and zinc oxide used for neutralisation is best determined by a blank or dummy test, or better by performing the process with a convenient measured amount of standard permanganate decomposed by hydrochloric acid. Besides the error from titrating in faintly acid solution, a further objection to acidifying with nitric acid is that the manganese dioxide precipitated

by titration collects as a film on the glass and obscures the end reaction.

Stone's modification is much easier and quicker than the regular Volhard method; not only because the evaporation to dryness with sulphuric acid is dispensed with, but also, as Mr. Stone points out, because in nitric acid solution the precipitated ferric oxide settles so readily and completely that the filtration from it may be omitted, the clear liquid being decanted from the precipitate. In sulphuric acid solution the precipitated ferric oxide does not settle readily enough for this, and thus considerable time is taken up in making folded filters, and the filter-paper used adds appreciably to the expense of the method.

Mr. Stone performs the neutralisation entirely with commercial zinc oxide, and this is doubtless the reason that his results have always been satisfactory, and he has noticed no necessity for the precaution of thorough neutralisation; for in neutralising altogether with zinc oxide, in the hurry of everyday work one would naturally get a large or a considerable excess of it used, even if not recognising the necessity for such an excess. And as to the precipitation of manganese with the iron, the work in this article would seem to show that to be an exceptional occurrence with nitric acid solution, although of frequent occurrence in sulphuric acid solution if caution be not used in the neutralisation. But as regards neutralisation, the writer considers it more advantageous to use sodium carbonate, or common sal soda first, finishing up with zinc oxide emulsion, for sal soda is much cheaper than commercial zinc oxide. But, as before mentioned, the manganese, organic matter, and proto-salts in these reagents, if any be present, must be allowed for.

Mr. Stone takes 100 c.c. for titration. But 250 c.c. is perhaps preferable on the score of greater accuracy. The writer finds it convenient to use permanganate of strength exactly 0.0056, taking always 3.75 grms. of the drillings for analysis. The reading of the scale on the burette then at once gives the percentage of manganese without calculation, except a division by ten.

For the convenience of those unfamiliar with the process details briefly follow, with the precautions found to be necessary in this article printed in italics:—3.75 grms. of drillings. Dissolve in 50 c.c. nitric acid, sp. gr. 1.20. Wash into a 500 c.c. measuring flask. Add about two thirds of the amount of sal soda solution necessary to a complete neutralisation. *If not cold, cool.* Add zinc oxide emulsion till solution stiffens, *avoiding an excess.* Dilute to about three-fourths of the capacity of the flask, mix, and let stand till the ferric oxide begins to settle. See that the solution is colourless: *Add considerable excess of zinc oxide emulsion.* Mix. Dilute to mark. Insert stopper. Mix. Transfer to dry beaker. Mix again. Let settle, and pour off 250 c.c. Titrate in 500 c.c. Erlenmeyer flask (first heating to boiling) with permanganate of strength 0.0056. Make the necessary deduction for impurities in the sal soda and zinc oxide. Divide the number of c.c. permanganate taken by ten. *Deduct 0.02 per cent.*

Following are some comparisons of results by this method with results by Volhard's method, gravimetric method, and colour method:—

TABLE XI.

No.	Volhard with	Stone with	Gravimetric.	Colour.
	all precautions.	all precautions.		
	Per cent.	Per cent.	Per cent.	Per cent.
1451	0.51	0.51	0.52	0.53
452	0.44	0.42	0.43	0.435
453	0.46	0.42 0.43	—	0.425
453	0.47	0.45	0.46	0.45
493	0.46	0.47	—	0.46
466	0.41	0.41	0.41	0.43
466	0.49	0.49	0.485	0.49
481	0.45	0.46	0.455	0.469
153	0.64	0.65	—	0.64

SOME EXTENSIONS OF THE PLASTER OF PARIS METHOD IN BLOWPIPE ANALYSIS.*

By W. W. ANDREWS.

(Continued from p. 248).

TIN gives a slightly volatile coating, showing a trace of brown when hot. Potassium thiocyanate, if dropped on the oxide and strongly heated, gives a pale yellowish green, infusible (compare lead). The slight volatility of tin oxide suggests a scale of volatility, of great use in describing the formation of the films on the tablets. The scale runs in the order of increasing volatility,—tin, zinc, cadmium, and mercury. Anything less volatile than tin might be classed as non-volatile.

The iodine solution yields a yellow, reddish brown when hot, the brown fading instantly. Potassium sulphide yields a black with a brown edge, which darkens on heating. Potassium cyanide discharges the colour, which turns black on heating, and when strongly heated shows the pale yellowish green (stannous thiocyanate, $\text{Sn}(\text{SCN})_2$; compare lead, bismuth, arsenic, mercury, and zinc). Water decomposes the film with formation of oxy-iodide.

Cobalt nitrate gives the bluish green, which is not so readily attacked by nitric acid as the zinc-green.

Antimony tri- or pentachloride yields with all tin salts a fine purplish blue-black coating, stable in the presence of acids. Potassium thiocyanate decomposes it when heated, and forms the pale green.

These tests with iodine, antimony trichloride, and with potassium thiocyanate, remove tin from the list of metals determinable with difficulty before the blowpipe. They can be depended on through a wide range of mixtures.

Lead yields *per se* a white and yellow; reddish brown when hot. All lead salts fuse into the tablet with the formation of lead plumbate, one of the constituents of glass. Potassium sulphide produces a brownish black, with reddish brown ring.

The iodine solution gives a film which is chrome-yellow, with a band of fainter yellow farther away (oxy-iodide?), and the assay is black. Potassium sulphide yields a spot with the reddish brown edge. Hydrochloric acid destroys the edge at once. Nitric acid wipes the spot off slowly, and sulphuric acid destroys the black and restores the yellow. The very volatile paler yellow on the outer edges is turned to a brighter colour by the same treatment (compare mercury). Potassium cyanide produces a slight paling of the sulphide colour. Potassium thiocyanate on the iodide film gives a black ring, which heated becomes a black spot (compare bismuth). Water wipes off the coating (compare mercury, arsenic, and silver).

The bromide film made by using potassium bromide and potassium hydrogen sulphate presents some interesting differences. It is white with a trace of yellow, the yellow fusing into the tablet. Potassium sulphide gives a spot, greenish for a moment and then black, on which potassium cyanide and potassium thiocyanate have no effect, but is partly destroyed by hydrochloric acid, more rapidly by nitric acid, and completely by sulphuric acid. Potassium thiocyanate, placed on the sulphide and heated, gives a black ring; with greater heat, a yellow; and still greater heat, a greenish grey ring. Potassium cyanide on the iodide film has no effect till heated; then a white. Potassium thiocyanate has no effect on iodide till heated; then a yellowish spot appears (compare tin). The sulphide heated becomes greyish black, on which nitric acid and the other acids have no effect (compare copper).

It is a good illustration of Carnelley's law of colour that in general the bromide film of any metal resembles

* From the *Journal of the American Chemical Society*, xviii., No. 10, October, 1896.

the iodide film of an element either in a higher series in its own family, or in the same series in another family toward the left in the natural classification. Thus the bismuth bromide film resembles the iodide film of antimony and lead. Lead bromide resembles tin and thallium iodide. Thallium resembles mercury, and mercury resembles silver in the same way.

Nitrogen with metaphosphoric acid in the nitrates yields an effervescence with the fumes, odour, and reactions of nitrogen tetroxide farther up the tablet, and in the cyanides the odour of hydrocyanic acid. Nitrates with carbonaceous matter yield ammonia, which will cause white fumes to rise from a spot on the tablet moistened with hydrochloric acid. Ross reports that any nitrogen compound with boric oxide yields a tough transparent bead, and, with metaphosphoric acid, purple in the reducing flame with manganese dioxide.

Vanadium gives with metaphosphoric acid a pale yellow in the oxidising flame, and in the reducing flame a green. (Ross).

Phosphorus.—A great desideratum in blowpipe analysis is a good test for this element and the phosphates.

Arsenic yields *per se* a brownish black with a white film falling farther away with odour of garlic and blue flame (compare thallium and tellurium). The iodide coat is white and pale yellow; the assay wholly volatile. Potassium sulphide, with a drop of hydrochloric acid, forms the yellow sulphide, little affected by acids. If oxalic acid be applied to a sulphide spot, and then hydrochloric acid, no effect is noticeable. The yellow will show up still better next day (compare antimony). If a drop of potassium thiocyanate be placed on the tablet about 1 inch above the assay, and between them a drop of nitric acid and the arsenical vapour be blown over them from the assay, there will generally be formed in the edge of the potassium thiocyanate spot a bright bluish green of unknown composition. All common acids except acetic destroy it. It shows well in the presence of salts of tin and antimony. When it does appear it is decisive for arsenic. This iodide film exhibits a very marked repulsive power for water, probably due to the arsenic oxide which forms with it. Potassium iodide with metaphosphoric acid yields more of the yellow than does the iodine solution.

Antimony *per se* yields a white and yellow band and white fumes. Potassium sulphide yields on this an orange-brown, which is quickly destroyed by a drop of nitric acid.

The iodide film is a fine orange-yellow, far away with yellow nearer the assay, and abundant white fumes. Potassium sulphide yields, especially when heated, an orange-red with a rich brown, and then a black beyond the spot. Hydrochloric acid slightly heated destroys it; nitric acid destroys it instantly, so also does its vapour. Potassium thiocyanate wipes the coating, but heated it yields a fine brown, which is permanent when exposed for months. Potassium cyanide wipes the coat. The orange-yellow sulphide spot, produced on the iodide film obtained with potassium iodide and metaphosphoric acid, is not so susceptible to the action of nitric acid, and is more rapidly destroyed by hydrochloric acid than the one described above.

If arsenic be present with antimony, there will be shown, inside the yellowish orange of the iodide film, a fine peachy pink, which is hard to wet. Stannic chloride yields with antimony, in most combinations, a purplish blue-black, which is remarkably stable (Haanel). It is now being collected in quantity, with a view to the determination of its formula. It will be seen that, with the blue with potassium thiocyanate, the rose-pink, and the reactions of the sulphide with hydrochloric, nitric, and oxalic acids, the presence of arsenic can be easily demonstrated in the presence of antimony, and, as far as experiment has gone, in the presence of any other substances.

Bismuth yields *per se* a yellow ring near the assay, and often a brittle globule. Potassium sulphide gives on the

white oxide a brownish black which nitric acid destroys, and on which hydrochloric acid has little effect till heated, when it removes it completely. Sulphuric acid has no effect. Potassium thiocyanate on the oxide produces a yellow ring, and heated a yellow spot turning black. (It is to be noted that potassium thiocyanate itself, when heated or treated with strong acids, shows on the tablet a fine yellow, which further heating renders colourless).

The iodide film is a splendid combination of chocolate-black, crimson, and yellow, the assay turning black. Potassium sulphide forms a chocolate black, soluble in nitric acid and not affected by sulphuric acid. The latter acid on the iodide film produces a black and a dull red edge. This is probably the sulphide formed by the reduction of the acid by the decomposition products of the potassium thiocyanate, which fall with the iodides. It has been noticed, however, to happen with no other metal than bismuth. This reaction is very useful in detecting small quantities of bismuth in the presence of other metals giving dark-coloured films (compare tellurium). Potassium thiocyanate on the iodide wipes it off, forming a yellow ring, but when heated it forms a black spot with a brown ring. Potassium cyanide also wipes the iodide, but when heated forms a dark grey spot. Glacial acetic acid wipes off the yellow and the crimson, but has no effect on the chocolate iodide.

Sulphur.—In looking for a better test for sulphur than the ordinary one with soda and a piece of silver, the stability at high temperatures and the two brilliant and characteristic colours of cadmium sulphide attracted attention, and the fact that it is easily formed in the presence of potassium cyanide. To a solution of cadmium bromide, potassium cyanide was added till precipitation took place, and then the solution of the precipitate as potassium cadmium cyanide. This, dropped on a fragment of the sulphide and heated, will show on the tablet near the assay a brilliant scarlet when hot, and bright yellow when cold. This is not affected by potassium cyanide (compare cadmium oxide). One great advantage of this is, that selenium and tellurium do not yield anything which can be confounded with these colours, selenium giving a greyish brown and tellurium a yellowish brown. Sulphates may be reduced by potassium cyanide, or by glycerol. A sulphide or sulphate fused with potassium cyanide will, if touched with a drop of ferric chloride, show in the tablet the pinkish red of ferric thiocyanate. The sulphur in the tablet causes no trouble.

Selenium and tellurium are further differentiated from sulphur by their characteristic films, which are tests of great delicacy. Twenty-seven varieties of complex sulphides, such as bournonite, tetrahedrite, stannite, &c., and all of the common sulphides and sulphates, were found to respond to this test at once.

Selenium yields *per se* with characteristic odour and flame a fine reddish brown, almost pure red on the outer edges and black on the inner edges near the assay. Potassium cyanide wipes it off, while potassium thiocyanate has no effect, except that if it be heated, a very stable red compound is formed ($KSeCN$?).

The iodide film forms in colour very similar to the *per se* coat, but more volatile. Potassium sulphide yields a yellow. Potassium cyanide wipes the iodide film off instantly, and therefore will reveal the presence of any other element not so affected, whose film might be hidden by the pronounced hues of the selenium film. Potassium thiocyanate has no effect, while it and heat wipe off most other coatings, and therefore will reveal the presence of selenium in obscuring associations, such as lead. Sulphuric acid shows a slight tendency to make this coating darker (compare bismuth).

(To be continued)

Determination of Acetone in Crude Acetones.—M. Klor (*Chem. Industrie*) finds the official method used in Germany inaccurate and misleading.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1896.

By WILLIAM CROOKES, F.R.S.,
and

PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, November 12th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Oct. 1st to Oct. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined one was recorded as "clear but dull," the remainder being clear, bright, and well filtered.

The excessive rainfall of last month has been succeeded by a nearly average fall in October. The 30 years' mean is 2.75 inches, and the actual rain has been 2.85, showing an excess of only 0.10 inch. Our bacteriological results are shown in the following table:—

	Colonies per c.c. 2691
Thames water, unfiltered	67
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	2
Ditto ditto lowest	19
Ditto ditto .. (12 samples) mean	671
New River water, unfiltered	4
New River water, from the Company's clear water well	742
River Lea water, unfiltered	14
River Lea water from the East London Com- pany's clear water well	

Our chemical and bacteriological results have recently been submitted to severe criticism in a report published by the London County Council. This is not the place, neither would time allow us to answer it in detail, but we cannot neglect the duty of correcting one or two of the most glaring mistakes.

In order to account for the alleged enormous bacterial contamination of the London supply, and therefore to condemn the efficiency of the treatment of the water by storage and filtration in opposition to our previous statements and results, the report declares that we do not conduct the bacteriological examination in a proper manner. The facts are exactly the opposite of what the report assumes. It is the mode of collecting and keeping the samples previous to the bacteriological examination, adopted by the reporters to the London County Council, that is unscientific. We rigidly follow the bacteriological methods of the originator of the process, viz., Dr. Koch, of Berlin, in the collection and treatment of the samples and in the plate development. Our results have for months been confirmed by the independent examinations of Dr. Edward Frankland. To get results entirely at variance with ours the samples must have been treated in an unscientific way for the purposes of such investigation. As to the five-hundredth

part of a grain in the gallon of suspended matter in the London supply, this need cause no scare. No natural or artificial filtration can avoid causing some amount of suspended matter. No supply from Wales, which must be subjected to chalk treatment and filtration before it could be supplied to London, could avoid containing as much, if not more, suspended matter, so that Londoners would in such future supply still have to consume 67.5 tons of peaty mud per annum. Our samples for bacteriological investigation contain all the suspended matter, and as long as the results show the relatively small proportion of microbes that our specimens have done, the public need not doubt the wholesome quality of the present London supply, and may safely discard the five-hundredth part of a grain per gallon of innocuous material in the form of suspended matter. It cannot be disputed that, in spite of all the allegations of increasing contamination in the valleys of the Thames and Lea, the water supplied to the Metropolis has improved during recent years instead of deteriorating; and with increased storage and effective filtration we do not doubt the present sources will continue to furnish a supply adequate in every way to the needs of the Metropolis.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 5th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. J. B. Knight, S. G. Rosenblum, and J. A. Craw were formally admitted Fellows of the Society.

The following certificates were read for the first time:—
Henry Edward Aykroyd, Ashwell, Toller Lane, Bradford;
William Ballingall, Ardarrock, Dundee; Charles Bathurst, Jun., Lydney Park, Gloucestershire; Lauritz Hansen Bay, The Grammar School, Carlisle; Charles Edward Browne, 2, Hinton Villas, Cheltenham; George Harold Cross, B.Sc., Balliol College, Oxford; William Duncan, Royal Dispensary, West Richmond Street, Edinburgh; Walter John Elliott, M.A., 5, Dover Place, Clifton, Bristol; John Thomas Fleet, Rugby, Warwickshire; George George, Regent Street, Kingswood, near Bristol; Arthur Croft Hill, Trinity College, Cambridge; Charles Alexander Hill, Hawthorns, South Road, Clapham Park; John William Hinchley, Baggeholme Road, Lincoln; William Trevor Lawrence, B.A., Ph.D., 57, Prince's Gate, S.W.; Robert Dexter Littlefield, 23, Wightman Road, Harringay, N.; Thomas Henry Lloyd, Penygraig, Pontypridd; Thomas William Lockwood, Heckmondwike; Edward Seaborn Marks, 111, Cromwell Road, S.W.; Arthur Stanley Mayfair, Avenue House, Beverley Road, Hull; William M. Miller, Prye Estate, Wellesley, Penang, Straits Settlements; Landon Clarence Moore, 19, Mecklenburgh Square, W.C.; Francis Ambrose Moss, Menzies, Western Australia; Herbert William Moss, Broken Hill Proprietary Company, Limited, Port Pirie, South Australia; Joseph Terrence de la Mothe, Grand Bacolet Estate, St. Andrew's Parish, Granada, West Indies; Alexander Henry Mitchell Muter, The Châtelet, Horley, Surrey; William Harrison Pearsall, The School House, Dalton-in-Furness; Henry William Potts, Euroa, Victoria; Frederick Belding Power, 21, Queen Square, Bloomsbury, W.C.; William Russell, Summerlie, Coatbridge, N.B.; Herbert Cecil Seabrooke, The Echoes, Grays, Essex; William Horace Sodeau, B.Sc., 25, Shore Road,

South Hackney, N.E.; Charles Thompson, Grammar School, Coatham, Redcar; William Henry Walker, Stafford Street, Willenhall, Staffs.; William Watson, M.A., School House, Kingsbridge, South Devon; Edwin Whitfield Wheelwright, B.Sc., Ph.D., The Oaklands, Warley, Oldbury, near Birmingham; John Harrison Wigner, Ph.D., 58, Breakspears Road, St. Johns, S.E.

Of the following papers those marked * were read.

*121. "The Constitution of the so-called Nitrogen Iodide." By F. D. CHATTAWAY, M.A.

From the beginning of the present century the black explosive compound formed when a solution of ammonia acts upon iodine, has almost continuously engaged the attention of chemists. No definite conclusion as to its constitution has, however, been arrived at, although from time to time different formulæ have been assigned to it, while, on account of its apparently variable composition, several distinct compounds have been supposed to exist.

The formulæ NI_3 , NI , NH_2I , NHI_2 , and NH_3NI_3 have been adopted by various chemists, while others have suggested that a series of different but allied substances exist, derived either from NH_3 , or a hypothetical substance, $\text{H}_3\text{N}:\text{NH}_3$, by replacement of hydrogen.

A number of experiments made with this substance with a view to the synthesis of hydrazine derivatives having given negative results, an investigation of the compound itself was undertaken.

Nitrogen iodide cannot be obtained dry in a condition suitable for analysis, so that all experiments have to be conducted with an unknown quantity and in presence of water. It is best prepared by adding a solution of iodine in potassium iodide to an excess of a strong solution of ammonia, when it is precipitated as a soft black powder.

Many analyses have shown that its composition does not vary according to the mode of preparation, provided that sufficient care is taken to remove unchanged ammonia, iodine, and the various products of the action. The substance always yields, on decomposition, ammonia and iodine, 1 mol. of ammonia being set free to 2 atoms of iodine. The variations of composition which have been observed are probably due to the substance not having been properly freed from ammonia or iodine, or to a decomposition of greater or less extent having taken place during the treatment of the substance after precipitation. If it be continuously washed with water, all the nitrogen can be removed as ammonium salts, practically pure iodine alone being left. This seems a sufficient explanation of the apparent existence of a series of compounds.

Nitrogen iodide has always been assumed to be a substitution derivative, mainly on the ground that in its preparation a large amount of ammonium iodide is formed.

This, however, is not the sole other product, ammonium hypoiodite also being produced, and, further, more than half the total iodine employed can be obtained in the nitrogen iodide produced. This could not happen if it were a substitution product.

A number of other facts, also, seem to show that it cannot be a substituted ammonia; for example, the invariable production of ammonia, and never of any nitrogen compound containing oxygen in its decomposition by various agents; its formation only from free ammonia, and never from ammonium salts; the fact that iodine does not substitute in NH_2 groups, and the production of ammonium iodide when it explodes.

Whenever it is decomposed, ammonia and iodine are always liberated; these may be free or partially combined together, or they may react with the agent effecting the decomposition. An excess of water decomposes the substance, yielding, if light be excluded, ammonium iodide and hypoiodite and free iodine. This action explains the decomposition of the compound by prolonged washing, and the consequent accumulation of iodine in the residue. The ammonium iodide and hypoiodite formed can dissolve

a little of the liberated iodine, but a certain amount cannot thus be taken into solution, and consequently remains behind mixed with the undecomposed compound. The percentage of iodine in the residue therefore continually increases, and ultimately only a small quantity of practically pure iodine is left behind.

Potash and soda very easily decompose the substance, liberating ammonia and forming iodide and hypoiodite, or if the solution be heated, iodide and iodate. The oxides of lead and silver suspended in water act similarly, ammonia is evolved, and iodide and iodate of the metal formed.

Finely-divided metals appear to assist the action of the water by combining with the liberated iodine.

Acids, generally speaking, decompose the compound, liberating iodine and ammonia, with the latter of which they combine. The action of hydrochloric acid is peculiar; it seems to form, at first ammonium iodide and iodine chloride.

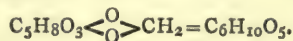
All substances capable of reacting with iodine at once decompose nitrogen iodide, yielding, in addition to ammonia, the same products that they yield with iodine itself.

Sulphuretted hydrogen forms ammonium iodide and hydriodic acid, while sulphur is precipitated. Sulphurous acid gives hydriodic acid and ammonium sulphate. Sodium thiosulphate liberates ammonia, and forms sodium iodide and sodium tetrathionate. The lower oxides of arsenic and antimony are converted into the higher, with liberation of ammonia and formation of hydriodic acid. Potassium cyanide sets free ammonia, and forms potassium iodide and cyanogen iodide.

On the whole, therefore, it seems that a single substance is formed by the action of ammonia on iodine, and that in this 1 atom of nitrogen is associated with 2 atoms of iodine. Whether the simplest formula that can be given to the substance is NHI_2 or NH_3I_2 can only be finally settled by a very careful investigation of all its reactions under the most varied conditions; but at present the formula NH_3I_2 seems best to accord with the reactions of the substance and express the known facts regarding it.

*122. "The Carbohydrates of Barley-straw." By C. F. CROSS, E. J. BEVAN, and C. SMITH.

This is a continuation of investigations which were the subject of a recent communication (*Trans.*, lxi., 804). The furfuroid carbohydrates isolated by acid hydrolysis from the cereal celluloses afforded evidence of the existence of a hexose-pentose series of tissue-constituents with a definite transition form corresponding with a pentose monoformal, i.e.,—



The methods leading to the recognition of this intermediate constitutional form have been applied to the plant taken at various stages of growth during the season 1896. The furfuroids were similarly isolated, and their constitution investigated by (1) osazones, (2) yeast fermentation, (3) the reaction with hydrogen peroxide previously described (*loc. cit.*).

The numbers obtained show a progressive variation. Thus, the osazones are at first of high melting-point (180—190°); the furfuroids are entirely broken down (fermented) by yeast in the neutralised solution, and the peroxide treatment shows negative results, i.e., no evolution of carbon dioxide. From the flowering stage onwards the osazones fall in melting-point; there is increasing resistance of the furfuroids to the action of yeast, and the characteristic reaction with hydrogen peroxide is observed, with increasing proportions of carbon dioxide formed.

These results point to the gradual transformation of a hexose into a pentose derivative.

At the same time the evidence is reviewed upon which these characteristic tissue constituents must be looked upon as having a special constitution or configuration *ab*

initio,—i.e., they are assimilated or elaborated in the first instance with the constitutional features which determine their characteristic decompositions, viz., (1) to furfural by the action of condensing acids, (2) to pentose derivatives as a normal incident of their life-history in the plant.

*123. "The Direct Union of Carbon and Hydrogen." By WILLIAM A. BONE and DAVID S. JERDAN.

The authors have continued and extended the experiments of which they gave some account to the Society six months ago (*Proc.*, clxii., 61) and now are in a position to discuss their results more fully.

In their first communication they stated that they had produced methane by passing a slow current of hydrogen, free from hydrocarbon impurities, over purified carbon heated to bright redness in a porcelain tube placed inside a Fletcher injector furnace.

The products of the union of carbon with hydrogen at the temperature of the electric arc have been more thoroughly studied. The electric arc was formed between terminals of purified gas carbon in an atmosphere of dry hydrogen contained in a glass globe standing in a trough over mercury. The arc was maintained in hydrogen for an hour or more, and samples of the gas were drawn off at the end of 5, 15, 30, 45, &c., minutes in each experiment. These were afterwards analysed in a modified form of the McLeod gas-analysis apparatus.

The gases almost always contained small amounts of hydrocyanic acid, due, no doubt, to the presence of a little nitrogen in the hydrogen employed. Acetylene was always present in considerable quantities, and, in addition to this and any other unsaturated hydrocarbon, appreciable quantities of methane were found.

*124. "The Explosion of Acetylene with less than its own Volume of Oxygen." By WILLIAM A. BONE and JOHN C. CAIN.

Continuing their earlier experiments (*Proc.*, cxlii., 170), the authors have exploded mixtures of acetylene with from 29 to 95 per cent of its own volume of oxygen in a leaden coil, some 5 metres long, having an internal diameter of 13 m.m. The coil was closed at each end by a steel tap, and at one end a stout glass firing piece, into which two platinum wires were fused, was fixed between the steel tap and the end of the coil. The other end of the coil was connected with a mercury manometer, so that the pressure change inside the coil after an explosion could be determined.

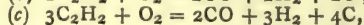
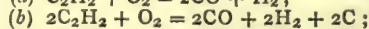
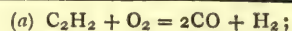
The coil was immersed in a bucket of cold water, which served to rapidly cool the gases in the coil after an explosion. The coil was filled with the explosion mixture at the ordinary atmospheric pressure by displacement: the mixture was then fired by an electric spark passed across the wires at the firing piece. After the products of the explosion had cooled down to the temperature of the water surrounding the coil, the tap nearest the manometer was opened, and the pressure of the gases inside the coil was read off. In all cases a considerable increase in pressure, varying from 260 to 370 m.m. of mercury, according to the mixture exploded, occurred.

Samples of the products of explosion were collected in each case, and these, together with the original mixtures of acetylene and oxygen, were carefully analysed in a modified form of the McLeod apparatus.

The products of explosion were found to consist chiefly of carbon monoxide and hydrogen, but in addition to these, small, but quite appreciable, amounts of acetylene and carbon dioxide were invariably present.

In their earlier experiments, the authors suspected the presence of a small amount of methane among the products of explosion of certain mixtures of acetylene and oxygen; a more rigid examination of the products has, however, shown that methane is not present in any appreciable quantity.

Further experiments indicate that, although the main resultant reaction may be expressed by such equations as



yet some steam is formed; this is evident from the fact that the ratio of the hydrogen to the carbon monoxide in the products is always less than the above equations require. Further, the presence of carbon dioxide in the products would be difficult to explain if no steam were produced.

The small percentages of nitrogen in the products of explosion are due to nitrogen contained in the original mixtures fired.

From these experiments it is evident that, when the electric arc is passed between carbon terminals in an atmosphere of hydrogen, acetylene and methane are both produced. Further, that the rate of formation of these two gases is fairly rapid during the first fifteen minutes of the experiment, after which the rate falls, and finally, after about half an hour, a state of equilibrium between the hydrogen, acetylene, and methane is attained. This equilibrium depends, to some extent, on the voltage employed.

These results led to the inference that methane and acetylene would both be decomposed by the electric arc, and that if the arc is passed long enough a similar state of equilibrium would be arrived at. This conclusion was fully borne out by subsequent experiments, in which pure acetylene or methane was subjected to the action of the electric arc passed between carbon terminals in the same apparatus as that employed in the experiments with hydrogen.

Both methane and acetylene are easily decomposed by the electric arc; during the first ten minutes of the experiment the gas (methane or acetylene, as the case might be) was very rapidly resolved into its elements, large flakes of carbon were formed in the neighbourhood of the terminals, and fell to the surface of the mercury below; the gas in the globe underwent a great increase in volume, much greater than could be accounted for by the mere expansion of the gas by the heat of the arc. A smoky flame rose from the terminals and filled the upper part of the globe. At the end of about ten minutes this extraordinary appearance subsided, after which the arc presented the same appearance as in the case of the hydrogen experiments. After the arc had passed for an hour, the experiment was stopped; samples of the gases were then collected and subsequently analysed.

The principal product in each case was hydrogen with about 9 per cent of acetylene, and small quantities of methane, nitrogen, and hydrocyanic acid. In the experiment with acetylene, a minute quantity of naphthalene was also formed.

125. "The Refraction Constants of Crystalline Salts." By WILLIAM JACKSON POPE.

Although a large mass of accurate data concerning the refraction constants and molecular volumes of crystalline substances possessing one, two, or three principal indices of refraction, has been collected, no successful attempt has hitherto been made to deduce a definite general relationship between the refraction constants and the composition of such salts. The author considers that the method used by Tutton, of calculating a single molecular refraction constant for biaxial crystalline substances as the arithmetic mean of the molecular refractions for the two extreme refractive indices, is not a logical one, but that the molecular refraction should be calculated from the mean of all three refractive indices in such cases; the molecular refraction of uniaxial salts should be calculated from a refractive index which is one-third of the sum of the extraordinary index, and twice the ordinary refractive index.

The molecular refraction constants obtained in this way are, within the limits of experimental error, of an additive nature, so that it becomes possible to compile tables of

atomic or equivalent refractions from which the molecular refraction of solid salts may be calculated additively in just the same way as is in general use for liquids.

The molecular refractions of some hundred or so salts have thus been calculated, both from the experimental data and from the table of atomic refractions, and comparison shows a good agreement between both sets of numbers.

The author shows that the molecular refraction of a solid salt, calculated as above described, is not quite the same as that of the salt in aqueous solution. The influence of the solvent is naturally eliminated by dealing with the solid salt alone, and a physical method of deriving valuable information respecting the constitution of solid substances is thus obtained.

126. "Compounds of Metallic Hydroxides with Iodine." By THEODORE RETTIE, B.Sc.

When iodine, dissolved in aqueous potassium iodide, is added to a solution of a magnesium salt, and potash is then carefully added to the mixed solutions, a dark brown precipitate is obtained. The author concludes that this and the somewhat similar precipitates obtained in an analogous manner with solutions of zinc, cadmium, and several other salts, consist of metallic hydrates with a variable quantity of iodine carried down with them, forming compounds resembling lakes.

127. "Economical Preparation of Hydroxylamine Sulphate." By E. DIVERS, M.D., F.R.S., and T. HAGA, D.Sc.

Sodium nitrite yields nearly its own weight of hydroxylamine sulphate when carefully sulphonated, by the addition of sodium sulphite, and hydrolysed. In sulphonating, the solution must be kept slightly below 0°, and the sodium carbonate be closely in proportion to the nitrite of 1 mol. to 2 mols. The hydrolysis in its second stage must not be carried out at a boiling heat, because then much hydroxylamine is destroyed. At 90–95° the hydrolysis is satisfactorily effected in two days. After neutralisation, the sodium sulphate is separated, and the hydroxylamine sulphate crystallised out. It is a non-deliquescent salt, soluble in three-fourths of its weight of water at 20°, and crystallises well.

128. "The Reduction of Nitrosulphates." By E. DIVERS, M.D., F.R.S., and T. HAGA, D.Sc.

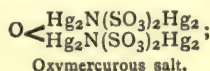
From a partly quantitative examination of the products of reduction of potassium nitrosulphate by sodium amalgam, it has been ascertained that they include hyponitrite, nitrous oxide, hydrazine, ammonia, nitrogen (probably), sulphite, sulphate, and amidosulphonate. Of 12 mols. of the salt it is estimated that six become amidosulphonate and nitrous oxide, four become sulphite and hyponitrite, and two become sulphate and partly hydrazine, partly nitrogen. The occurrence of hydrazine was discovered by Duden, in 1894; that of sulphate and amidosulphonate is new. The production of sulphate by the sodium is regarded by the authors as another proof that nitrosulphates have not a sulphonic constitution. The formation of amidosulphonic acid is attributed to the salt being a sulphate of a hydrogenisable radicle, and in this respect like no other known sulphate.

129. "Imidosulphonates. Part II." By E. DIVERS, M.D., F.R.S., and T. HAGA, D.Sc.

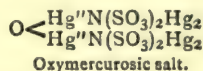
Through the kindness of Dr. Raschig the authors have been able to compare the contents of Berglund's Swedish papers on Imidosulphonic Acid and Amidosulphonic Acid, with their own results, which appeared in the *Journal* in 1892 (*Trans.*, lxi., 943). They find that they have succeeded fairly well in making their own work supplementary to his and not a repetition of it. Where there has been overlapping some interesting points are raised.

The normal sodium salt had been prepared by Berglund but only by indirect methods, not by the sulphonation of sodium nitrite. The $\frac{2}{3}$ normal salt he did not prepare.

There is disagreement as to the composition of the oxymercuric salt, and in the present paper new work is submitted, establishing fully, in the authors' judgment, the correctness of their formula, which makes the salt contain the bivalent group $-\text{HgOHgOHg}-$, found also in the oxymercuric sulphate, sulphite, and imidosulphonates. What the authors have described as the calcium sodium salt, Berglund mistook for the normal calcium salt. Among the new salts described in this paper are the true normal calcium and the true normal strontium, as well as the $\frac{2}{3}$ normal calcium salt. Berglund also mistook, it appears, the strontium sodium salt for the normal strontium salt. The mercuric sodium salt he duly recognised as such. The mercuric calcium salt has now been prepared, as also a compound of it with mercuric chloride, analogous to apatite, imidosulphonic acid holding the place of phosphoric acid. An oxymercurous salt described is of interest on account of the contrast it shows between imidosulphonic acid and amidosulphonic acid, the latter, like ammonia, resolving mercurous salts into metal and mercuric salts. Lastly, mercurous salts have been prepared, remarkable in exhibiting a substitution, to varying extent, of the mercurous radicles in the preceding salt by mercuric radicles. The limit of this substitution is expressed in the following formulæ:—



Oxymercurous salt.



Oxymercurous salt.

(To be continued).

CORRESPONDENCE.

LUCIUM.

To the Editor of the Chemical News.

SIR,—In the *CHEMICAL NEWS* (vol. lxxiv., p. 159) there is an article on Lucium, in which my name is mentioned in confirmation of the properties of lucium as determined by P. Barrière. There must be in this matter a misunderstanding which I should wish to clear up. Certainly, in concert with my son-in-law Dr. E. Hintz, I have concerned myself during the last year almost continually with the chemistry of the rare earths (being induced by the "Glow-light" lawsuits), but I have published no communications which could justify the assumption that a new element like lucium was contained in the thorite which has been submitted to me.—I am, &c.,

DR. R. FRESENIUS.

Wiesbaden, November 17, 1896.

The Jubilee of Science Teaching in the City of London School.—A strong committee has been secured to promote the "Hall Memorial Fund" in celebration of the jubilee of the introduction of science teaching at the City of London School. This fund is to be available for instituting or founding scholarships for the encouragement of chemistry and experimental science at the City of London School. Among those who have consented to serve on the committee are Dr. W. H. Perkin, Mr. Alexander Mortimer, the Rev. Dr. Abbott, Sir Frederick Abel, Alderman Sir H. E. Knight, Professor Garnett, Mr. A. T. Pollard, Colonel Sewell, Mr. C. J. Wilkinson-Pimbury, Mr. J. Spiller, and Mr. Henry Durham, the last two acting as hon. secretaries. Subscriptions towards the fund will be received and acknowledged by Mr. A. Mortimer, 1, Paper Buildings, Temple, and Mr. J. Spiller, 2, St. Mary's Road, Canonbury.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 18, November 2, 1896.

New Researches on the Tubercles of Leguminous Plants.—Ch. Naudin.—The author combats experimentally the theory that leguminous plants derive their supplies of nitrogen from the vital action of bacteria inhabiting the nodosities of their roots. These nodes are most abundant on the roots of the papilionaceous division of the legumens. According to Nobbe and Hillmer the species chiefly if not exclusively concerned is *Bacterium Beyerinckii*. Prof. Schneider, of the University of Minneapolis, says the fixation of nitrogen is effected by six species which he places in the genus *Rhizobium*.

On Röntgen's Phenomenon.—Abel Buguet.—It is known that the X rays may be recognised behind a screen exposed to a Crookes tube even if such screen is sufficiently opaque to entirely protect a photographic plate to which it is closely applied. Such an opaque disc of lead exposed between a Crookes tube and a photographic plate rather far from the latter gives a circular spot surrounded by a shaded halo. On arranging such a disc at some centimetres from a tube before a sensitive plate at the distance of 10 or 15 c.c., and carrying the exposure rather far, I have been able, in a series of experiments, to obtain an impression over the entire photographic surface. On arranging upon this plate a series of pins distributed over the surface and all perpendicular to it, I obtained the projections of these pins in white upon grey. All these projections are directed from the centre to the circumference towards the degraded halo already mentioned by several experimentalists. It seems, therefore, impossible to admit that the X rays lean towards the margin of the screen to penetrate behind it, since, if such were the case, the projections of the pins would be directed from the circumference towards the centre of the halo. I cannot admit willingly that the disc of lead may be regarded as transparent in the existing conditions, for blocks of various thickness closely superposed on the disc at various points of the surface on the side of the Crookes tube left no traces on the proof. It seems to be that the peculiar state of space on the free track of the X rays reaches the neighbouring regions which are masked by the screen. The new properties are transmitted with all their characters, those especially which decide the direction of the projection of the pins, characters which fix the direction of the X rays if we aim at comparing the Röntgen radiations with those of light. This transmission of properties is, moreover, an important function of distance, as results from the relative narrowness of the halo. The movement of the molecules of the air, rendered active by radiation, and conveying their new properties behind the opaque screen, does not seem to me capable of explaining the fixity of the phenomenon. In a series of experiments a sheet of lead covered a part of the base of a cylinder of paraffin of 15 c.m. in height resting upon a sensitive plate. It was thus separated from the photographic plate by the paraffin at one end and by an equal layer of air at the other.

Formation Heat of Lithium Hydride.—M. Guntz.—Lithium hydride is a very stable substance, differing greatly in its properties from potassium and sodium hydrides.

Uniformity of the Distribution of Argons.—Th. Schloesing, jun.—As far at least as living beings are concerned argon may be regarded as very indifferent; nevertheless its inutility is not really demonstrated. We may conclude with greater certainty than heretofore that argon is, like oxygen and nitrogen, uniformly distributed in the

atmosphere, and that it is found normally in the proportion of 1·184 per cent of nitrogen and oxygen.

Method of the Reproduction of Double Silicates of Potassium and other Bases.—André Duboin.—We are tempted to approximate glucina to magnesia rather than to alumina on account of the solubility of glucina in potassium fluoride.

French Essential Oil of Roses.—J. Dupont and J. Guerlain.—The French oil of roses contains along with terpenic products an ether endowed with a strong levorotatory power.

Use of the X Ray for Anatomic Research.—C. Remy and G. Contremoulins.—Will be inserted in full.

MEETINGS FOR THE WEEK.

MONDAY, 30th.—Society of Arts, 8. "The Use of Gas for Domestic Purposes" (Cantor Lectures), by Prof. Vivian B. Lewes.

WEDNESDAY, Dec. 2nd.—Society of Arts, 8. "The Teaching of Economics," by W. A. S. Hewins, M.A.

THURSDAY, 3rd.—Chemical, 8. Ballot for Election of Fellows. "Constitution and Colour," by Arthur G. Green. "Some Experiments on Sea-water," by E. Sonstadt. "Derivatives of a-Hydrindone," by C. Revis and F. S. Kipping, Ph.D., D.Sc. "Notes on Nitration," by H. E. Armstrong. "2:3-Bromobetanaphthol," by H. E. Armstrong and W. A. Davis. "Derivatives of Nitrobetanaphthols," by W. A. Davis. "Morphotropic Relations of Betanaphthol Derivatives," by W. A. Davis. "Researches on Tertiary Benzenoid Amines," by Miss O. Evans.

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1932.

PROXIMATE CONSTITUENTS OF COAL.*

(Concluded from p. 262).

THE benzene solution, after removal of the benzene, leaves a dark resinous mass, which, when ground, forms a brown powder, which is dissolved not only by benzene and acetone, but also by ether, chloroform, glacial acetic acid, phenol, and nitrotoluene, but is insoluble in carbon disulphide, petroleum ether, and water. The solutions of this body are all dark brown, almost black, and from these it is always deposited in an amorphous condition. The analysis of this substance gave the following results, from which a formula, $C_{30}H_{22}Cl_8O_{10}$, has been deduced:—

(a) 0.364 grm. gave 0.578 grm. CO_2 , and 0.086 grm. H_2O				
0.293	"	0.411	"	AgCl = 34.67 per cent Cl.
(b) 0.357 " 0.571 " CO_2 , and 0.087 grm. H_2O .				
0.322	"	0.448	"	AgCl = 34.42 per cent Cl.
	a.	b.	Means.	Calculated for $C_{30}H_{22}Cl_8O_{10}$.
C	43.29	43.60	43.44	43.64
H	2.62	2.70	2.66	2.66
Cl	34.67	34.42	34.54	34.29
O	19.42	19.28	—	19.41
	100.00	100.00	—	100.00

From the alcoholic extraction there was obtained, after removal of the alcohol, a brown solid, very similar in appearance to that obtained from the benzene solution. The results of the analysis of this substance most nearly accord with a formula $C_{24}H_{18}Cl_4O_9$.

(a) 0.420 grm. gave 0.740 grm. CO_2 and 0.114 grm. H_2O .				
0.463	"	0.451	"	AgCl = 24.05 per cent Cl.
(b) 0.386 " 0.680 " CO_2 and 0.104 grm. H_2O .				
0.569	"	0.550	"	AgCl = 23.88 per cent Cl.
	a.	b.		Calculated for $C_{24}H_{18}Cl_4O_9$.
C	48.05	48.05		48.66
H	3.01	2.99		3.04
Cl	24.05	23.88		23.96
O	24.89	25.08		24.34
				100.00

From the material left after extraction with benzene and alcohol, which is sparingly soluble in hot alcohol, but soluble in acetone, two substances have been obtained which contain a smaller proportion of chlorine than the above, and from the analytical results appear to have the formulae $C_{22}H_{14}Cl_3O_5$ and $C_{25}H_{20}Cl_3O_8$. The deep yellow acid filtrate from which the oxidised and un-oxidised coal had been removed was shaken out with ether; the ethereal solution appears to contain some trichloroacetic acid. The aqueous solution, after extraction with ether, when concentrated to a small bulk, deposits crystals of potassium chloride, &c., coloured yellow by a colouring matter which is removed by acetone. The acetone solution, on evaporation, gives a reddish viscous liquid, which is dissolved by ether and alcohol, but is insoluble in benzene.

The analysis of the residue left after the evaporation of

acetone showed it to contain some mineral matter, which was left as ash when the substance was burnt. Owing to the small amount at disposal, a further purification was not attempted. The determination of the carbon, hydrogen, and chlorine gave the following:—

(a) 0.4132 grm. gave 0.6460 grm. CO_2 and 0.1414 grm. H_2O .				
0.4158	"	0.2584	"	AgCl. Cl = 15.36 per cent.
(b) 0.357 " 0.5608 " CO_2 and 0.125 grm. H_2O .				
0.4402	"	0.2706	"	AgCl. Cl = 15.20 per cent.
0.426	"	0.015	"	Ash = 3.52 per cent.
	a.	b.		
C ..	42.61 per cent	42.82 per cent		
H ..	3.80 "	3.88 "		
Cl ..	15.36 "	15.20 "		
Ash ..	—	—		3.52 per cent

Calculating the percentages of carbon, hydrogen, and chlorine for the substance free from ash, we get amounts corresponding to the formula $C_{33}H_{36}Cl_4O_{20}$, as shown below:—

	a.	b.	Calculated for $C_{33}H_{36}Cl_4O_{20}$.
C =	44.18	44.39	44.29
H =	3.94	4.03	4.02
Cl =	15.92	15.76	15.88
O =	35.96	35.82	35.81
	100.00	100.00	100.00

Although the action of hydrochloric acid and potassium chlorate on the coal is a slow one, it is much more thorough in its attack than other oxidising agents tried. The coal left after treatment and removal of oxidised product with acetone, when submitted to a second treatment with acid and chlorate of potash, is still further attacked and converted into products similar to those formed in the first instance, and it appears that the proportion of oxidised product increases with each successive oxidation. To study the mode of action, 10 grms. of the coal were boiled with dilute acid and 20 grms. of chlorate of potash, added in small quantities at a time, the action continued for forty-four hours. The dried product was found to have increased by 21 per cent in weight, and of this 62.7 per cent was dissolved by acetone. The residue left after treatment with acetone weighed 5.27 grms., which was again oxidised for forty hours. Of the dried product 74 per cent was removed by acetone, and the remaining 1.26 grms., after a third and similar treatment, gave a product from which acetone dissolved some 77.8 per cent, leaving 0.32 grm. of coal-like insoluble residue.

The analysis of the coal after it had been treated four times with these reagents shows an increased percentage of carbon and hydrogen and the presence of a trace of chlorine.

From the above it is evident that the coal substance is powerfully attacked by hydrochloric acid and potassium chlorate, but the products of this action are for the most part complex substances, from which at present but little information can be derived as to the nature of the materials from which they are formed. These bodies appear to be acidic in properties, and form dark brown solutions with caustic alkalis and ammonia, from which metallic salt solutions, such as barium chloride, lead nitrate, silver nitrate, &c., precipitate out dark coloured gelatinous salts, which are difficult to obtain in a state of sufficient purity for analysis. The attempts to obtain information as to the constitution of these chlorinated compounds have up to the present yielded no satisfactory results.

The composition and physical properties of these chlorinated compounds recall those described by Messrs. Cross and Bevan in their investigations of jute, for example, the substance described by these authors as tetrachlorobastin ($C_{38}H_{36}Cl_8O_{18}$), from which they have obtained protocathechuic acid by fusion with potash.

* Report of the Committee, consisting of Sir I. Lowthian Bell (Chairman), Professor P. Phillips Bedson (Secretary), Professor F. Clowes, Dr. Ludwig Mond, Professor Vivian B. Lewes, Professor E. Hull, Mr. J. W. Thomas, and Mr. H. Bauerman. Read before the British Association (Section B), Liverpool Meeting, 1896.

The treatment of cannel coal with hydrochloric acid and potassium chlorate results in the production of compounds similar to those obtained from the coal of the Hutton seam, the oxidation product soluble in alcohol contained some 24.13 per cent of chlorine.

A sample of bitumen submitted to a similar treatment gave a product from which ether dissolves about two-thirds, the ethereal solution on evaporation leaving a dark viscous residue, which was found to contain 11.06 per cent of chlorine.

Whilst postponing for the present the further study of these chlorinated compounds, Mr. Smythe has begun the investigation of the action of hydrochloric acid and potassium chlorate in "brown coal." For this purpose samples of brown coal were obtained from Brühl, near Cologne; this variety of coal is much more readily attacked than the coal from Durham; it is also noteworthy that while the dry oxidised product from the latter weighs more than the coal, in the case of the brown coal there is a notable decrease in the weight. Further, there is a much larger proportion of the oxidised product soluble in acetone, as the following details of an experiment with 10 grms. of finely ground coal show.

Ten grms. of brown coal boiled for twelve hours with dilute hydrochloric acid and 20 grms. of potassium chlorate; the insoluble mass was filtered off, washed, and dried. The dried solid weighed 6.82 grms.; of this 72.4 per cent was soluble in acetone. The portion insoluble in acetone, viz., 1.88 grms., was treated for twelve hours more with hydrochloric acid and potassium chlorate, giving a solid product of 1.49 grms., of which 79.8 per cent was dissolved by acetone. The chlorinated compounds formed in this manner are very similar in appearance to those obtained from the Hutton seam coal, and probably of a similar character. The crude solid left after the evaporation of the acetone was found to contain some 22.93 per cent of chlorine.

The investigation of these substances, as also the products formed by the oxidation of brown coal with solutions of potassium permanganate, are still in progress.

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SOME EXTENSIONS OF THE PLASTER OF PARIS METHOD IN BLOWPIPE ANALYSIS.*

By W. W. ANDREWS.

(Concluded from p. 265).

TELLURIUM gives *per se* with flame and odour a brownish black with a white film falling nearer the assay (compare arsenic). Sulphuric acid, if gently heated, shows an effervescent pink of tellurium sulphate. Acetic acid wipes off this coat (compare cadmium). So do the potassium cyanide and ammonia fumes. The iodide film is brownish and purplish black, less brown than the *per se* coat. Potassium cyanide wipes it off in the cold. Potassium thiocyanate has no effect on the purple (compare thallium), and slightly dissolves the brown, and if nitric acid be added a yellow appears. Potassium sulphide darkens the coating a little. Sulphuric acid acts as on *per se* film.

Chromium yields an assay which is dark green when hot and a fine green on cooling. This test can be made very delicate. Metaphosphoric acid gives similar colours.

Molybdenum yields *per se*, and especially by flaming, an ultramarine coating. The oxide film, which forms when the iodine solution is used, comes better by flaming of the film and in presence of vapours of sulphuric acid. A potassium thiocyanate spot, over which the vapours from the assay have swept, exhibits a splendid hyacinthine pink. Metaphosphoric and sulphuric acid vapours aid its formation. It is probably molybdenum thiocyanate ($\text{Mo}(\text{SCN})_2$). If potassium thiocyanate be added to the assay this colour will spread all around the edges of the blue, extending to a distance of two inches from the assay. This very delicate reaction is of special interest, from the fact that it shows that part of the potassium thiocyanate, or at least the radical thiocyanogen, travels undecomposed that distance over the tablet, and that all these films are formed in the presence of moist potassium thiocyanate or thiocyanogen vapours, which will account for the behaviour of some of the films. This pink is decolourised by ammonia, not restored by nitric acid. Sulphuric acid dropped on the tablet will form a blue ring (MoSO_4). Metaphosphoric acid yields blue or bluish green glasses according to the degree of saturation (Ross). Tungsten and uranium in metaphosphoric in the reducing flame yield, the former a blue and the latter a green glass (Ross).

Fluorine.—If a fluoride be mixed with phosphoric acid and a piece of glass be laid on the tablet about 2 c.m. away from the assay, a fine etched semicircle will show itself after the heating of the assay. The radius of the semicircle is about 3 c.m. long.

* From the *Journal of the American Chemical Society*, xviii., No. 10, October, 1896.

Manganese yields with metaphosphoric acid a glass which is violet hot and cold, colourless in the reducing flame, and turning green on the addition of an excess of soda (Chapman, Ross).

Chlorine.—Chlorides, bromides, and iodides of the alkali metals yield *per se* white coatings, which may be distinguished from other white coatings by their flames and by the action of a small quantity of the coating scraped together and mixed with the metaphosphoric acid cobalt glass, which will remain blue on cooling.

A compound of chlorine if mixed with metaphosphoric acid and heated, in the reducing flame (if oxy salt), will cause white fumes to rise from a spot moistened with ammonia situated about 2 c.m. above the assay. If a copper salt be present in the glass or near it, so that copper chloride vapours are formed, and these are allowed to sweep over a spot of nitric acid and then over one of potassium thiocyanate, near the assay a yellowish brown coating of cupric chloride will form with an azure blue flame, and beyond the potassium thiocyanate spot a fine blue-black, very volatile (see copper).

A bromide with potassium cyanide added to it and the fused mass laid upon a copper glass and a drop of nitric acid added, a fine red will show itself. Bromides with metaphosphoric acid saturated with copper, upon blowing, yield a fine and very volatile reddish violet coating. If a bismuth salt be exposed to the hot vapours, it will yield a yellow coating. The spot on the tablet moistened with starch paste, not too near the assay, will turn yellow.

Similarly treated iodine compounds yield violet vapours, a violet in the glass appearing with effervescence, and with copper salt they yield a white coating, with bismuth scarlet and chocolate, and with starch a bluish black.

Iron gives an iodide film too delicate in colour to show up well, either on the white or the black surface. Its presence can be shown by a red colouration after blowing hydrochloric acid vapours over the tablet, to turn all ferrous compounds into ferric, and then adding a drop of potassium thiocyanate to the coating. It is difficult to obtain plaster of Paris sufficiently pure not to give this reaction for iron. Such reaction can, however, be readily distinguished from that given by an assay. Metaphosphoric acid gives a luminous yellow when hot, which is perfectly colourless when cold. A drop of acid on this to produce ferric compounds, followed by a drop of potassium thiocyanate, will show the red of ferric thiocyanate, which is decolourised by phosphoric acid, but not by hydrochloric acid. Made in this way, this test is not too delicate to show the iron of composition. An assay of iron treated with a drop of sulphuric acid and heated will show on the tablet a film of Venetian red.

Cobalt yields a glass blue hot, and violet cold; permanently blue if alkali be present. Boron trioxide acts similarly. With the iodine solution a spot around the assay turns pink, then deep blue on heating, and then black.

Nickel with boron trioxide separates as green fragments, which may be gathered by solution of the glass in water, and then the separated nickel (as any nickel compound) will yield in metaphosphoric acid, a reddish brown when hot and amber yellow when cold (Ross).

Palladium gives a dull blue-black film with the iodine solution, which is very characteristic. The assay turns dull black.

Osmium yields *per se* a greenish black. The iodide film is a combination of olive green, dove, and slate colours, with red appearing around the lower edges. The edge of the coating nearest the assay shows greenish brown, and the assay itself will be closely surrounded with an iridescent black film. Potassium sulphide turns the coating somewhat darker, which, heated, becomes a brownish film, which is wiped off by hydrochloric and nitric acids, and not affected by sulphuric acid and potassium cyanide. On the iodide films sulphuric acid has no effect; potassium thiocyanate has none till heated, and then it turns brown. Hydrochloric and nitric acids

remove the film. Potassium thiocyanate dropped on the tablet over an inch from the assay before the coating is deposited, will, when the vapours sweep over it, turn to a fine brick red, destroyed by potassium cyanide and the acids.

Potassium bromide and potassium hydrogen sulphate give a pinkish brown (compare copper). Potassium sulphide produces a grey not affected, which turns darker on being heated, destroyed by acids, and not affected by potassium cyanide.

Iridium yields with the iodide solution an indistinct brownish yellow coating and a potassium thiocyanate spot, which in tint resembles the molybdenum spot, but it is covered with dots of darker pink.

Platinum gives an infusible grey film. Ruthenium and rhodium are being investigated.

All these reactions have been obtained from a large number of the compounds of each element except in the cases of osmium, indium, and iridium. The writer will be glad to hear of any cases in which they fail, and to receive specimens of combinations which cannot be unlocked by this method. One grm. weight of any alloy is sufficient. The next work to be undertaken is to exhaustively determine the lowest percentage of any metal which can be determined with certainty in the presence of one, two, or any number of other metals, to describe the characteristic effect that one metal has on the coating yielded by another when they are deposited together, and to determine the value of each metal as an interfering element.

Covered Tablets.

The tablets are easily cut with a knife, and therefore they can be used in various ways. Open tube work can be performed on a tablet if a groove be cut lengthwise of a tablet and laid upon another, groove down. A small pit for the assay is cut in the lower one about one centimetre from the end. The groove is cut so that its narrowest part is just above the assay pit, and from that point to the lower end it flares into a half funnel form, and into this the flame is blown. By regulating the size of the groove at its narrowest part the amount of air which will flow over the assay may be regulated. This method is of great use when very small quantities of precipitates are to be tested. For instance, five-tenths m.grm. of arsenious oxide gave in one experiment a narrow coating one-half inch long on each tablet. This gives ample opportunity for making confirmatory tests. Various reagents may be placed along the groove to be acted on by the vapours, gold leaf for mercury, potassium cadmium cyanide and lead acetate for hydrogen sulphide fumes, starch, bismuth, and antimony solutions for iodine, copper sulphate for chlorine, &c.

If a coating be made, or a small piece of volatile salt be placed in a small pit in the tablet and a thin tablet be placed over it, it is found that if potassium sulphide, or potassium thiocyanate be dropped on the upper tablet, and the flame be directed upon the drop, they will pass through the tablet, and reactions will take place away from the air. After a few seconds blowing the upper tablet will be found to be floating on a layer of hot gas, which flows between the two smooth surfaces. Tin and arsenic, and other substances easily oxidising in the air, form their sulphides very readily under these conditions. Potassium thiocyanate forms sulphides. It is in this way possible, by using ammonium hydroxide or hydrochloric acid, to form the sulphides in the presence of moist acid or alkaline vapours.

Other methods of using the tablets will be described later.

In teaching research methods, the plaster of Paris method is one of the finest instruments to use with beginners. In the course of an hour a student will have been able to make from twenty to forty different tests, and without any delay in preparing solutions, or in waiting for filtration to take place, he will have produced

the oxide, sulphide, chloride, bromide, and iodide of a given metal, and will have noted their colours, manner of deposition, volatility, solubility in several reagents, and the behaviour of the assay itself at high temperatures, and will have ransacked his vocabulary to find terms to describe the phenomena in his written notes. His skill in manipulation and his powers of observation are kept in liveliest exercise, and his independence developed, for it is quite possible to give each student in a large class his own problem. In no other laboratory work do the compelled acts of judgment follow each other as rapidly. There are many problems which may be set requiring reference to standard chemical literature, and many simple, and some very difficult equations of reactions to be written.

Not the least valuable consideration from an educational standpoint is the æsthetic quality of the work. All the coatings are symmetrical in form and beautiful in shading, and many of them in brilliancy of hue and in delicacy of shading rival the most splendid colours of flowers. This gives added interest to the work, and is of great value since adult students are so frequently found to be greatly deficient in the colour-sense, as children are not. There has not been opportunity to compare the shades of these films with the descriptions given in the "Standard Dictionary." When this has been done exact training can be given in colour language also.

Apology is offered for publishing the results of this research at this stage, when so many unsolved problems stand along its path, but this much is given in order that the practical value of these reactions and methods may be put to the test.

THE CHEMISTRY OF THE CONSTITUENTS OF MONASITE.

By PAUL DROSSBACH.

As it is known the chief constituents of the monasite form a by-product of the manufacture of thorium nitrate. They serve for the production of easily fusible glasses capable of resisting fluctuations of temperature, whilst didymium is used for decolourising glass.

The monasites of commerce form three varieties without reference to that from Norway—(1) Brazilian monasite, fine polished grains of an amber-yellow; (2) Carolina monasites from Cleveland county, well-developed sharply angular yellow crystals mixed with the integrating constituents of the local laterite from which monasite has been formed (chrome-iron, titanite, garnet, and zircons); (3) Monasite of the north-eastern spurs of the Blue Mountains, dark-brown crystals from the size of a hemp seed to that of a pea. The last-mentioned variety is the material of the present work.

There were used each time 3000 to 4000 kilos. of the mineral carefully prepared and very finely ground. The mean composition of the mineral was as follows:— $\text{Ce}_2\text{O}_3 = 21.4$ per cent; $\text{La}_2\text{O}_3 = 14$ per cent; $\text{Di}_2\text{O}_3 = 28.8$ per cent; oxides of the erbium group = 1.5 per cent; thorium oxide, $\text{ThO}_2 = 8.0$ per cent; alien oxides of the cerium group about $\frac{1}{2}$ per cent. The residue consisted of phosphoric acid, silica, and the mechanical impurities of monasite. The specific gravity of the mineral was constant at 5.13. The geological details of the monasite deposits will be considered elsewhere.

Methods of Separation.—The monasite, very finely ground, was opened up in the well-known manner, and after the feebly-basic thorium has been fractionated out, the lye obtained by lixiviation with cold water is at once mixed with a large excess of concentrated sulphuric acid. On the application of heat the sulphates of cerium, didymium, and lanthanum (very sparingly soluble in dilute sulphuric acid) separate out, whilst the sulphates

of the true erbium group remain in solution. A saturated solution of sodium sulphate is formed by partial neutralisation with soda. In this liquid the sulphates of the cerium elements are perfectly insoluble, and separate out in the state of double salts.

The sulphuric solution of the erbium elements is now advantageously precipitated with oxalic acid in order to eliminate iron and phosphoric acid. The elaboration of the oxalic precipitate will be described below.

Separation of Cerium from Lanthanum and Didymium.

—The procedure depends on the fact that cerium sesquioxide as a hydrate or in a solution kept constantly neutral is oxidised by permanganate according to the equation—

$$3\text{Ce}_2\text{O}_3 + 2\text{KMnO}_4 + \text{H}_2\text{O} = 6\text{CeO}_2 + 2\text{KOH} + 2\text{MnO}_2.$$

The procedure takes practically the form that the mixture of oxides is precipitated with ammonia in an aliquot part of the liquid, and the cerium is titrated with permanganate. We then add to the main quantity a small excess of permanganate and the calculated quantity of alkali, when the cerium falls down quantitatively but accompanied with a didymium constituent.

The main quantity of the didymium can be extracted by a little dilute nitric acid, and then the cerium with stronger acid, leaving a residue of manganese dioxide. The cerium dioxide solution is mixed, according to Auer, with ammonium nitrate, and the double salt which is easily crystalline is obtained by evaporation.

Separation of Lanthanum and Didymium.—The fractionation with ammonia formerly proposed was not successful, since both lanthanum and didymium oxide expel ammonia from its salts. It is superseded by Auer's oxide process. Equally good results are obtained more simply by fractionating the nitrate solutions with soda lye. Soda lye is added to the general solution until the supernatant liquid is free from any absorption-spectrum. The solution then contains the bulk of the lanthanum free from didymium; the precipitated hydrate in turn on digestion with crude didymium lye gives up gradually all its lanthanum to the latter liquid. The lanthaniferous didymium lye is added to a subsequent portion.

Scission of Didymium.—I have not tried the method followed by Auer and Schottländer, and refer solely to that fraction of didymium which is deposited along with the cerium.

The original monasite-didymium displays a great number of absorption bands; one between A and B, a narrow stripe between B and C, a similar one to the left of D, a broad band to the right of D, a narrow stripe to the left of E, a stripe at E to the left of B, three delicate stripes and a broad band between F and G.

The didymium ingredient precipitated along with cerium shows merely the narrow stripe to the left of D, as also two strong sharp bands to the right of D. Details are reserved for a future investigation.

Separation of the Erbium Elements.—The above mentioned oxalic precipitate, free from didymium, is converted into hydrate by treatment with potassa lye (not soda lye), dissolved in nitric acid, and the nitric solution precipitated with magnesia; the filtrate contains all the yttrium if the precipitation is repeated twice, and the precipitate all the ytterbium, erbium, and probably a new oxide. If the mixture of oxides is fractionated either according to Auer's original method or according to the basic nitrate procedure mentioned under lanthanum, almost all the ytterbium is collected in the first fractions, since ytterbium in this process, according to Auer, is precipitated before erbium. All these first fractions as far as they show no trace of absorption are collected together. That we have here to do with ytterbium can in first place be judged only from the atomic weight. The statements published on ytterbium do not permit us to decide. But as the periodic system assumes two oxides whose atomic weights fall very near that of ytterbium, it is in consequence of the want of sharp reactions very possible here a new oxide may be present.

The finely coloured eriferous liquid is now so long precipitated with soda lye (much diluted and added very gradually until the supernatant liquid no longer shows any trace of an absorption spectrum). The erbium hydroxide is dissolved in sulphuric acid, and the pure sulphate is obtained in splendid rose-coloured crystalline crusts. The mother-liquor contains considerable quantities of the oxide described below.

The solution freed from erbium may be conveniently again precipitated with oxalic acid in order to remove impurities which have accumulated or which have been derived from the reagents.

The oxalates may be converted into oxides or hydrates by ignition or by treatment with potassa lye. It is advisable to precipitate fractionally the above sulphatic mother liquor (poor in erbium), and again to precipitate with oxalic acid the filtrate when freed from erbium. The hydrate thus obtained is again converted into a nitrate, and as its concentrated solution often still shows traces of an erbium spectrum, this is eliminated in the manner mentioned. If the elimination of the didymium has not been previously effected with care, didymium lines are still displayed. Didymium is, however, so strongly basic that in the following operations it always adheres to the last portions. The nitrate solution thus obtained free from erbium was submitted in two portions, A to six-times fractionation with soda-lye, B to five times repeated fractional crystallisation of the sulphates by admixture with sulphuric acid and concentration.

The mean atomic weight of the elements perfectly free from erbium as calculated from the sulphates is 114 if the oxide is R_2O_3 . In the fractionated precipitation of the nitrates the first fraction still showed erbium and had the atomic weight 157; the second, third, fourth, and fifth had respectively the atomic weights 100.5, 98.5, 98.5, 100.5; the sixth fraction was 109.7. The last still retained didymium and lanthanum, as the further treatment showed. The two intermediate sulphate fractions yielded a similar result, whilst the terminal members showed higher atomic weights (Er, Di).

The four intermediate fractions showed in accordance, along with the reactions of the group, the following behaviour:—The sulphate is relatively easily soluble in water, and only concentrated solutions yield crystalline crusts when heated. The solutions yield no absorption-spectrum. The oxalate is soluble in solutions of the alkaline oxalates. Hydrogen peroxide and ammonia throw down a white precipitate (peroxide?). The carbonate, like the hydrate, is readily soluble in an excess of alkaline carbonate.

Only the solution of ammonium carbonate gradually deposits carbonate, but not on the addition of ammonia. The oxalate is soluble in carbonates. It is distinguished from thorium by its strong basicity and by the solubility of the double sulphates of the alkaline metals.

As an element of the above named properties and of an atomic weight close upon 100 finds no place in the atomic system, further investigations must determine whether a different valence than that assumed belongs to the above-named constituent of monasite, or if we have to do with a unitary substance. This investigation the author reserves to himself.—*Berichte*, xxix., No. 15, p. 2452.

COLOUR PHOTOGRAPHY.*

By Professor G. LIPPMANN, Membre de l'Institut (France).

THE problem of colour photography is as old as photography itself. The desire of fixing the colours as well as the design of the beautiful image thrown on the screen of the camera, very naturally occurred to the earliest ob-

servers. Since the beginning of this century three distinct solutions of the problem have been realised.

The first solution, not quite a complete one, is founded on the peculiar properties of a silver compound, the violet subchloride of silver. E. Becquerel (1860) converted the surface of a daguerreotype plate into this silver compound, and by projecting on it the image of the solar spectrum, and other objects, obtained good coloured impressions. Poiteven substituted paper for the silver plate as a substratum. No other substance has been discovered that can play the part of the subchloride of silver. Moreover, the image is not fixed, in the photographic sense of the word; that is, the coloured impression is retained for any length of time in the dark, but it is blotted out by the action of daylight. The reason of it is this: the Becquerel images are formed by coloured silver compounds, which remain sensible to light; so that they are destroyed by the continued action of light, in virtue of the same action which gave them birth. Despite the numerous experiments made by Becquerel, Poiteven, Zenker, and others, no substance has been found that is capable of destroying the sensibility of the subchloride for light without, at the same time destroying its colour.

The second method for colour photography is an indirect one, and may be called the three-colour method. It was invented in France by Ch. Cros, and at the same time by M. Ducos du Hauron (1860). German authorities claim the priority of the idea for Baron Bonstetten. Three separate negatives (colourless) are taken of an object through three coloured screens. From these three positives (equally colourless) are made; and, lastly, the colour is supplied to these positives by means of aniline dyes or coloured inks. Thus three-coloured monochromatic positives are obtained, which by superposition give a coloured image of the model. In the ingenious process lately invented by Prof. Joly, the three negatives, and apparently the corresponding three positives, are obtained interwoven on one and the same plate. The three-coloured method can give a very good approximation to the truth, and has probably a great future before it. We may call it, nevertheless, an indirect method, since the colours are not generated by the action of light, but are later supplied by the application of aniline dyes or other pigments. Moreover, the choice of these pigments, as well as of the coloured screens through which the negatives have been obtained, is in some degree an arbitrary choice.

The third and latest method by which colour photography has been realised is the interferential method, which I published in 1891, and the results of which I beg to lay before you. It gives fixed images, the colours of which are due to the direct action of the luminous rays.

For obtaining coloured photographs by this method, only two conditions are to be fulfilled. We want (1) a transparent grainless photographic film of any kind, capable of giving a colourless fixed image by the usual means; and (2) we want a metallic mirror, placed in immediate contact with the film during the time of exposure.

A mirror is easily formed by means of mercury. The photographic plate being first enclosed in a camera slide, a quantity of mercury is allowed to flow in behind the plate from this small reservoir, which is connected with the slide by a piece of india-rubber tubing. The slide is then adapted to the camera, and the action of light allowed to take place. After exposure the slide is separated from the camera, the mercury reservoir lowered so as to allow the mercury to flow back into it; the photographic plate is then taken out, developed and fixed. When dry, and examined by reflected light, it appears brilliantly coloured.*

The sensitive film may be made either of chloride, iodide, or bromide of silver, contained in a substratum

* A Lecture delivered at the Royal Institution of Great Britain, April 17, 1896.

* The glass of the photographic plate has to be turned towards the objective, the film in contact with the metallic mirror.

either of albumen, collodion, or gelatine. The corresponding developers, either acid or alkaline, have to be applied; the fixation may be cyanide or bromide of potassium. All these processes I have tried with success. For instance, the photograph of the electric spectrum now projected before your eyes, has been made on a layer of gelatino-bromide of silver, developed with amidol, and fixed with cyanide of potassium.

As you see, bright colour photographs may be obtained without changing the technique of ordinary photography: the same films, developers, and fixators have to be employed; even the secondary operations of intensification and of isochromatisation are made use of with full success. The presence of the mirror behind the film during exposure makes the whole difference. From a chemical point of view nothing is changed, the result being a deposit of reduced silver left in the film, a brownish, colourless deposit. And yet the presence of a mirror during exposure causes the colourless deposit to show bright colours. Of course we want to know how this is done; we require to understand the theory of those colours.

We all know that colourless soap-water gives brilliant soap-bubbles; the iridescence of mother-o'-pearl takes birth in colourless carbonate of lime; the gorgeous hue of tropical birds are simply reflected from the brownish substance which forms the feathers. Newton discovered the theory of these phenomena, and subjected them to measurement; he invented for the purpose the experiment called by the name of Newton's rings. Newton showed, as you know, that when two parallel reflecting surfaces are separated by a very short interval, and illumined by white light, they reflect only one of the coloured rays which are the constituents of white light. If, for instance, the interval between the reflecting surfaces is only $2/10,000$ of a millimetre, violet rays are alone reflected, the rest being destroyed by interference: that is, the two surfaces send back two reflected rays whose vibrations interfere with one another, so as to destroy every vibration except that which constitutes violet light. If the interval between the reflecting surfaces be augmented to $3/10,000$ millimetre, the destruction of vibration takes place for every vibration except that of red light, which alone remains visible in this case.

If we consider now this photograph of the spectrum, and especially the violet end of the image, we find that this is formed by a deposit of brown reduced silver. In the case of an ordinary photograph, this deposit would simply be a formless cloud of metallic particles; here the cloud has a definite stratified form; it is divided into a number of thin equidistant strata, parallel to the surface of the plate, and $2/10,000$ m.m. apart. These act as the reflecting surfaces considered by Newton, and as they are at the proper distances for reflecting violet rays, and these alone, they do reflect violet rays.

The red extremity of the photograph is equally built up of strata which act in a like manner; only their distance intervals here amount to $3/10,000$ m.m., and that in the proper interval for reflecting red light. The intermediate parts of the spectral image are built up with intermediate values of the interval, and reflect the intermediate parts of the spectrum.

The appearance of colour is therefore due to the regular structure above described, imprinted on the photographic deposit. The next question is—How has this very fine, peculiar, and adequate structure been produced?

It is well known that a ray of light may be considered as a regular train of waves propagated through the ether, in the same way as waves on the surface of water. The distance between two following waves is constant, and termed the wave-length; each sort of radiation, each colour of the spectrum, being characterised by a particular value of the wave-length. Now when a ray of light falls on a sensitive film, this train of waves simply rushes through the film with a velocity of 300,000 kilometres per second; it impresses the film more or less strongly,

but leaves no record of its wave-length, of its particular nature or colour, every trace of its passage being swept out of form by reason of its swift displacement. The impression therefore remains both uniform and colourless. Things change, however, as soon as we pour in mercury behind the plates, or otherwise provide for a mirror being in contact with it. The presence of the mirror changes the propagated waves into standing waves. The reflected ray is, namely, thrown back on the incident ray, and interferes with its motion, both rays having equal and opposite velocities of propagation. The result is a set of standing waves—that is, of waves surging up and down, each in a fixed plane. Each wave impresses the sensitive film where it stands, thus producing one of these photographic strata above alluded to. The impression is latent, but comes out by photographic development. Of course the distance between two successive strata is the distance between two neighbouring waves; this, theory shows, is exactly half the wave-length of the impressing light. In the case of violet, for instance, the wave-length being $4/10,000$ m.m., half the wave-length in the above quoted distance of $2/10,000$ m.m.; this, therefore, is at the same time the interval between two successive standing waves, in the case of violet light the interval between two successive photographic strata, and at last it is the interval required to exist, according to Newton's theory, for the said strata reflecting violet rays, and making these alone apparent when illuminated by white light.

The colours reflected by the film have the same nature and origin as those reflected by soap-bubbles or Newton's rings; they owe their intensity to the great number of reflecting strata. Suppose, for instance, the photographic film to have the thickness of a sheet of paper (one-tenth of a m.m.), the fabric built in it by and for a violet ray is five hundred stories high, the total height making up one-tenth of a m.m. Lord Rayleigh, in 1887, has proved *à priori* that such a system is specially adapted to reflect the corresponding wave of light.

(To be continued).

Detection of the Benzoyl Radicle in Organic Substances.—E. Léger (*Bull. Soc. Chim. de Paris*).—The characteristic is an odour of peppermint, or, in other words, of benzoic ethyl ester.

Detection of Tartaric Acid by means of Resorcin.—G. Denigés. — Mohler's solution of resorcin prepared with concentrated sulphuric acid is not very permanent. To avoid this defect Denigés dissolves 2 grms. white retorcin in 100 c.c. water, and adds $\frac{1}{2}$ c.c. concentrated sulphuric acid. This solution is quite permanent. If oxidising agents are present, they are first reduced with zinc and sulphuric acid.—*Zeit. Anal. Chem.*

A Reagent for Sugar.—A. Conrad (*Apoth. Zeitung*). —Cane-sugar, grape-sugar, and levulose in solutions containing 0.1 per cent, if boiled for three minutes with 0.1 resorcin and 1 c.c. hydrochloric acid, yield a colour rose to carmine. To detect milk-sugar in cane-sugar the author boils 1 grm. milk-sugar in 10 c.c. water, adds 0.1 grm. resorcin, 1 c.c. hydrochloric acid, and boils for five minutes. In the absence of cane-sugar the solution does not turn red.

Recognition of Mineral Acids in presence of Acetic Acid.—G. Griggi. —(*Chemiker Zeitung*). The author spreads on a flat porcelain capsule 1 c.c. of the liquid in question, especially vinegar. He then adds one drop of an alcoholic solution of magenta, containing 25 grms. magenta dissolved in 100 c.c. of alcohol at 90 per cent by volume. On mixing both liquids, if any acetic acid is present, the colour of the magenta remains unaltered, but if a mineral acid is present, the liquid takes a dirty yellow colour. On neutralising with an acid the original colour of the magenta is restored.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 5th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

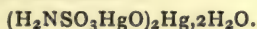
(Continued from p. 269).

130. "Amidosulphonic Acid." By E. DIVERS, M.D., F.R.S., and T. HAGA, D.Sc.

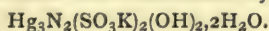
Except in the field of organic chemistry, nearly all that is known of amidosulphonic acid and its salts we owe to its discoverer, Berglund. Outside his work, in 1876, there is only to be mentioned that Fock has described its crystals and Raschig discovered a simple and excellent, though costly, method of preparing it by sulphonating hydroxylamine.

Of the additions now made by the authors to the knowledge of this acid, the following are the most prominent. Amidosulphonic acid is largely precipitated from its solutions by sulphuric acid. This fact makes the preparation of the acid from sodium nitrite very easy. Its preparation from this source is also very inexpensive; for when the nitrite has been sulphonated, and the product hydrolysed, the solution neutralised, and sodium sulphate crystallised out, there only remains to add some concentrated sulphuric acid, in order to get amidosulphonic acid almost pure, and in quantity equal in weight to at least three-fourths of the nitrite worked upon.

Amidosulphonic acid combines with mercuric oxide only to form a basic insoluble compound. The acid precipitates the same compound from a solution of mercuric nitrate, which it can completely decompose, its mercury compound being insoluble in dilute nitric acid. More remarkable is the fact that this compound is soluble in alkalis. In its degree of basicity it agrees with the oxymercuric sulphate, sulphite, and imidosulphonates, and may therefore be formulated as—



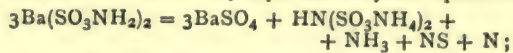
But, since potassium hydroxide dissolves it without decomposing it, and that, regarding its amidosulphonic acid as an amine, it behaves exactly like a mercurammonium compound with Pesci's reagent (ammonium bromide), it may be taken to be—in alkaline solution at least—a sulphonated mercurammonium hydroxide,—



Amidosulphonic acid shows, again, a likeness to ammonia in serving to prevent precipitation of silver nitrate by potassium hydroxide. When the amidosulphonate is not in excess, a bright, ochre-yellow, colloidal substance can be precipitated from solutions of moderate dilution. Much water decomposes it, and forms with it a colloidal brown solution (apparently of silver oxide). Its composition seems to be expressed by the formula $AgHNSO_3K$. Double decomposition between silver nitrate and potassium amidosulphonate does not take place when their solutions are mixed. The normal silver salt is well known.

The first action of heat upon amidosulphonic acid is very interesting. It melts at 205° , but not without decomposing, to a liquid which solidifies to a transparent vitreous mass, on cooling. The properties of this mass, which is formed without gain or loss in weight to the acid, show it to be composed of ammonium pyrosulphate and ammonium pyro-imidosulphonate in molecular proportions, along with 7 to 10 per cent of unchanged acid. This transformation of the acid by heat is a striking example of intra-molecular decomposition and of cumulative re-solution in the direction of ammonia and water for hydration and salt formation. The behaviour of the mixed pyro-salts, when further heated, is described in the author's paper, but must be passed over here. Anhydrous salts of amidosulphonic acid are largely converted

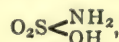
by heat into imidosulphonates and ammonia, but also into sulphates and gases. The decomposition of the barium salt, for instance, is nearly represented by the equation—



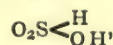
but it is only this salt that yields nitrogen sulphide.

131. "Molecular Conductivity of Amidosulphonic Acid." By J. SAKURAI.

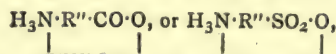
The molecular conductivity of amidosulphonic acid was determined by means of a Kohlrausch's universal bridge; the result shows that it is a strong monobasic acid, being nearly comparable with iodic acid. The author compares, at different dilutions, the degree of dissociation of amidosulphonic acid,—



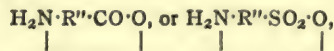
with that of sulphurous acid,—



at the same dilutions, and shows that the former acid is much stronger than the latter. This result, he points out, is interesting from the fact that the influence of the NH_2 group upon the strength of organic acids generally is just of the opposite character, as is well known, and gives a confirmation of the view already published (*Proc.*, 1894, cxxxvii.) on the constitution of glycocin and other organic amido-acids. The fact that organic amido-acids are weaker than the non-amidated acids, whilst amidosulphonic acid is stronger than sulphurous acid, of which it is the amido-derivative, shows that mere presence of NH_2 does not diminish the strength of an acid. The difference can only be understood by assuming that, in the case of the former class of acids, the nitrogen of the basic group, $-R''NH_2$, is in combination with the hydrogen of the acid group, $-CO_2H$ or $-SO_3H$; thus—



the dissociation of these molecules into H, on the one hand, and—



on the other, occurring to a much less extent than in the case of the non-amidated acids, which dissociate into H and $R'CO_2$ or $R'SO_3$.

Finally, the author considers the dilution formulæ of electrolytes recently proposed by Rudolphi (*Zeit. Phys. Chem.*, 1895, xvii., 385) and van 't Hoff (*Zeit. Phys. Chem.*, 1896, xviii., 300), and shows that his results are in agreement with these formulæ.

132. "The Physiological Action of Amidosulphonic Acid." By OSCAR LOEW, Ph.D.

Amidosulphonic acid, applied as its calcium or sodium salt, proves to be noxious to the life of phænogamous plants, but not to Algæ or to the lower Fungi. It is not poisonous to the lower aquatic forms of animal life, such as Infusoria, Rotatoria, Copepoda; and, from experiments made by Prof. D. Takahashi, it proves to be also not poisonous to vertebrate animals, such as the dog and the frog. That its poisonous action should be confined to flowering plants is a point of much interest.

133. "How Mercurous and Mercuric Salts change into each other." By S. HADA, B.Sc.

By the results of numerous experiments, the ways are shown by which mercuric salts in presence of water become mercurous, and mercurous salts become mercuric. Very much has been observed already by others concerning such a common subject, but the statements based on past experience have been uncertain and even contradictory, and nearly every point has had to be worked out anew.

It has now been ascertained that a cold solution of mercuric nitrate shaken with mercury is at once and fully converted into one of mercurous nitrate, one of mercuric acetate into mercurous acetate, and one of mercuric chloride into simple water and a precipitate of mercurous chloride. As was better known, moist mercuric sulphate or phosphate quickly becomes all mercurous salt, with evolution of heat, when rubbed with mercury.

Mercurous nitrate in boiling water becomes mercuric nitrate and metallic mercury, which distills with the steam. Other mercurous salts, soluble or insoluble, e.g., the chloride, behave similarly. This dissociation proceeds also at lower temperatures, even to a measurable extent at 40°, in the case of the nitrate, on condition that, by a current of air, the mercury vapour is carried away.

Mercurous salts, in solution or moist, are also all dissociated at the common temperature by strong daylight, the acetate allowing the effects of dissociation to be very clearly observed.

Mercurous nitrate, when free from its mother-liquor, is a stable salt, unchanged in the air if not exposed to bright light. In solution in the dark, in a closed vessel, it is also stable even in an atmosphere of oxygen. There is no evidence that this or any other mercurous salt, whether in solution or only moist, is oxidisable in the air at common or only moderately elevated temperatures. What has been supposed to be the effect of oxidation, as in Mialhé's experiments, is the effect of dissociation. Mercurous oxide alone is oxidisable.

Mercurous salts, in presence of water, and best when in solution, oxidise in air or oxygen at a temperature of 150°. Thus, mercurous chloride can be largely, if not wholly, changed by oxidation into mercuric chloride in presence of hydrochloric acid. When mercurous chloride, boiled with hydrochloric acid under atmospheric pressure, becomes mercuric chloride, it does so by dissociation, not by appreciable oxidation.

Mercurous nitrate in water at the common temperature, but in strong daylight, becomes mercuric salt by reduction of its own nitric acid to nitrous acid. Exposure in an open vessel, or to an atmosphere of mercury vapour, or even to undiluted oxygen, retards the progress of the change by keeping down the quantity of nitrous acid which otherwise increases with time. An atmosphere of carbon dioxide favours—that is, does not impede—the change.

Mercurous nitrate also freely becomes mercuric nitrate and nitrite when kept in solution at 150° under pressure.

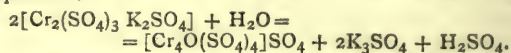
Mercurous oxide both oxidises and dissociates at the common temperature, as has been shown by Barfoed. Exposed to the air, it increases or lessens in weight, according to conditions. Shut up in an atmosphere of moist air, it gains in weight, dissociation being checked and oxidation favoured. Exposed with large surface to the open air, it loses in weight, for then dissociation and volatilisation of the mercury go on faster than oxidation of the undecomposed mercurous oxide.

134. "The Effect of Heat on Aqueous Solutions of Chrome Alum." By MARGARET D. DOUGAL.

As is well known, the colour of an aqueous solution of chrome alum, when heated, changes from violet or purple to green, and, on evaporating, the green solution yields a green non-crystalline mass.

The author has made a series of observations on the relative rates of diffusion of green and violet solutions of the same initial strength, which go to prove that the green diffusate contains less chromium and more sulphuric acid than the violet diffusate, which is compatible with the assumption that the green solution contains a colloidal, and therefore slowly diffusing chromosulphuric acid. This conclusion is in harmony with the results recently arrived at by Monte, and inferred by Whitney, that when a solution of chrome alum is heated it is resolved into a mixture of potassium sulphate, chromylsulphuric

acid, and free sulphuric acid, according to the following equation:—



Experiments have also shown that solutions of chrome alum, after heating, are less dense than the unchanged or violet solutions, the expansion being due, in all probability, to the production of the free sulphuric acid.

135. "On the Hydrolysis of Ethylic Dicarboxylglutamate." By H. W. BOLAM, B.Sc., Ph.D.

It was found impossible to prepare glutamic acid in quantity from ethylic dicarboxylglutamate, following the directions of Conrad and Guthzeit (*Annalen*, ccxxii., 254). Attempts to prepare this acid from β -oxyglutaric acid likewise failed. No oxyglutaric acid, such as v. Pechmann and Jenisch (*Ber.*, 1891, xxiv., 3250) describe, could be isolated from the product of the reduction of acetone-dicarboxylic acid by means of sodium amalgam.

It was found that ethylic dicarboxylglutamate underwent, on boiling with alkalis (baryta and caustic potash), a remarkable decomposition, the products being malonic acid and formic acid. The yields of glutamic acid are still further reduced by the action of alkali, it being shown that oxyglutarates (possibly β -) are formed. The decomposition is effected on boiling with a one per cent solution of baryta; in the cold, on the other hand, no such decomposition was observed with even a 20 per cent solution of caustic potash. On saponifying the ethylic dicarboxylglutamate with acids no such decomposition takes place; here, however, syrupy products, presumably both α - and β -oxyglutaric acids and the lactone acid, butyrolactone carboxylic acid, are formed, and these hinder the crystallisation of the glutamic acid. Using 11 per cent hydrochloric acid, and observing certain precautions in boiling, and on evaporation, yields of from 50 to 60 per cent of glutamic acid are got.

Ethylic benzylidicarboxylglutamate undergoes no decomposition on boiling with alkalis, nor does the benzylglutamic acid thus formed show any tendency to form oxy-acids. It is supposed that other alkyl substituted ethylic dicarboxylglutamate behave similarly, and it is suggested that an explanation of the decomposition of the simple ethylic dicarboxylglutamate is to be found in the presence of the hydrogen atom replaceable by a metal, and that, further, only ethers having such a replaceable hydrogen atom may be expected to show an analogous decomposition on boiling with alkalis.

136. "The Periodic Law." By R. M. DEELEY.

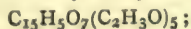
In this paper it is pointed out that the manner in which the elements group themselves varies according to the comparative importance which is attached to their several physical and chemical properties. The elements have generally been grouped in accordance with their most striking chemical properties. When thus grouped the author shows that many of them do not fall in with a regular periodic system, and the arrangement would seem to indicate that quite a number of elements of small atomic weight remain to be discovered. On the other hand, when they are grouped in accordance with the periodic changes in the values of many of their physical properties, the result is much more satisfactory. As an example, the refraction equivalents are instanced, helium being shown to fill a blank for a missing element (pointed out in a previous paper), whilst argon falls most naturally between sodium and fluorine. The periodic arrangement proposed makes the list of elements of smaller atomic weight than iodine complete, if we discount the possibility of the existence of a whole group of inert elements of lower atomic weights respectively than hydrogen and the alkali metals.

137. "The Colouring-matters occurring in various British Plants." Part I. By A. G. PERKIN and J. J. HUMMEL.

Formerly numerous British plants were employed in

dyeing, and at present in remote districts, notably the Highlands of Scotland, some are still used for this purpose. Many of these have been found sufficiently strong in colouring-matter to warrant their chemical examination.

The colouring-matters of the yellow wallflower, Cheiranthus cheiri.—An aqueous extract of the flowers when digested with acid deposits a precipitate of colouring-matter; this was found to consist of two substances which could be separated readily, owing to the difference of their solubilities in alcohol. The more soluble product which was obtained as yellow needles, had the formula $C_{15}H_{10}O_7$, yielded an acetyl compound,—



colourless needles, m. p. $189-191^\circ$; when decomposed with fused alkali, protocatechuic acid and phloroglucin were produced. It was found to be *quercetin*.

The sparingly soluble colouring-matter, $C_{16}H_{12}O_7$. minute, yellow needles, gave an acetyl compound, colourless needles, melting at $195-196^\circ$, and, when acted upon by hydriodic acid, it yielded *quercetin*, and one molecule of methylic iodide. It was thus a *quercetin monomethyl ether*. Though closely resembling rhamnetin it is not identical with it, for acetylramnetin melts at $184-185^\circ$; and for it is proposed the name *isorhamnetin*.

The colouring-matter in white hawthorn blossoms, Crætagus oxyacantha, was obtained as yellow needles having the formula $C_{15}H_{10}O_7$. Its acetyl compound, colourless needles, melted at $189-191^\circ$, and, when fused with alkali, phloroglucin and protocatechuic acid were formed. There could be no doubt as to its identity with *quercetin*. It is most probable that these colouring-matters exist in the above plants as glucosides. This point will be studied at a later date.

138. "Position-isomerism and Optical Activity; the Comparative Rotatory Powers of the Dibenzoyl and Ditoluylltartrates." By PERCY FRANKLAND, Ph.D., F.R.S., and FREDERICK MALCOLM WHARTON, A.I.C.

The authors have recently shown (*Trans.*, 1896, 1309) that the rotatory effect of the para-toluyll radical is greater than that of the meta- and this again greater than that of the ortho-toluyll group. This relationship, they have pointed out, is in harmony with the relative position of the centre of gravity in these several groups, for assuming that the centre of gravity of the benzene ring is the geometrical centre of a regular hexagon, it is obvious that in the ortho-arrangement of the toluyll group the centre of gravity is somewhat nearer, in the meta-arrangement somewhat further, and in the para-arrangement still further than that geometrical centre from the carbonyl carbon atom by means of which the ring is in each case attached to the asymmetric carbon atom of the tartaric acid. They have now investigated the relationship subsisting between the rotation of these toluyll compounds and the corresponding benzoyl derivatives. To this end they have studied the rotation, over a wide range of temperature, of methylic and ethylic dibenzoylltartrate, with the result that they have found that the rotation of the benzoyl compound is in each case intermediate between that of the corresponding ortho- and meta-toluyll derivative. This is also the relative position of the centre of gravity in the respective rings with regard to the carbonyl carbon atom by means of which they are attached.

Methylic and ethylic dibenzoylltartrates, like the corresponding ditoluylltartrates, were found to possess rotations which are very sensitive to temperature, the high negative value of the rotation diminishing with rise of temperature. In this condition ethylic dibenzoylltartrate was found to exhibit the phenomenon of a maximum rotation. This maximum is situated in the vicinity of its melting-point, the rotation values diminishing more and more as it is examined in a state of superfusion at temperatures further and further below its melting-point.

139. "Researches on the Terpenes. VII. Halogen Derivatives of Camphor." By J. E. MARSH and J. H. GARDNER.

When camphor is treated with a mixture of bromine and phosphorus trichloride at the ordinary temperature, it yields a mixture of two isomeric compounds, of the formula $C_{10}H_{14}Br_2$, α - and β -tribromocamphene hydrobromides. The two compounds are separated by crystallising from light petroleum.

α -Tribromocamphene hydrobromide crystallises from chloroform in large colourless crystals; it melts at 168° , and its specific rotatory power $[\alpha]_D = +90.3^\circ$.

β -Tribromocamphene hydrobromide melts at $143-144^\circ$, and has the rotatory power $[\alpha]_D = +7.6^\circ$.

When boiled with sodium methylate in methyl alcohol both the above-mentioned compounds react in the same way, losing hydrobromic acid, and yielding the same tribromocamphene, $C_{10}H_{13}Br_3$.

Tribromocamphene melts at $75-76^\circ$, and has the specific rotatory power $[\alpha]_D = +33.5^\circ$.

The action of bromine and phosphorus trichloride on other substances has been examined. Borneol yields the same compound (m. p. 168°) as camphor. Ordinary turpentine gives a new compound of the formula $C_{10}H_{14}Br_2$, which crystallises in colourless needles melting at 150° .

When pentachloride of phosphorus acts on camphor in the cold, two isomeric chlorocamphene hydrochlorates are obtained, which may be separated by petroleum ether. One of these compounds, α -chlorocamphene hydrochloride, appears to be in all respects identical with that originally described by Spitzer, having the melting-point 155° and specific rotatory power $[\alpha]_D = -9^\circ$.

β -Chlorocamphene hydrochlorate is very slightly soluble in petroleum ether, and crystallises from the hot solution in large, colourless, hard crystals; that obtained by Spitzer forms small, soft, binding crystals. The new isomeric compound melts at 168° , and has the rotatory power $[\alpha]_D = -27.7^\circ$. When boiled with zinc dust and glacial acetic acid it yields chlorocamphene, $C_{10}H_{15}Cl$, a colourless solid of low melting-point, which distils at 202° and has a specific rotatory power $[\alpha]_D = -29.7^\circ$.

Spitzer's compound also yields a chlorocamphene by the same treatment, but it is difficult to say whether it is identical with or different from the derivative of the β -compound. It is usually contaminated with higher chlorinated products.

When chlorocamphene is acted on with strong sulphuric acid it dissolves, with evolution of hydrogen chloride, and on pouring the solution into water a liquid is obtained, which can be distilled in steam. It has a strong camphorous smell, and burning taste. It boils at 250° , and has the composition $C_{10}H_{16}O$. The examination of its properties is not completed, but it appears to be a saturated tertiary alcohol, and is probably a hydroxyl-derivative of camphene.

140. "Derivatives of Camphenesulphonic Acids." By ARTHUR LAPWORTH, D.Sc., and FREDERIC STANLEY KIPPING, Ph.D., D.Sc.

This paper contains an account of the study of the two camphenesulphonic chlorides which are obtained as by-products in the preparation of camphorsulphonic chloride; the properties of these substances, and those of all their more important derivatives, have been briefly described in previous notes (*Proc.*, 1895, 57; 1896, 152).

141. "Preparation of Dimethylketohexamethylene and Experiments on the Synthesis of Dimethylhexamethenylmalonic Acid." By F. STANLEY KIPPING, Ph.D., D.Sc., and W. B. EDWARDS.

The appearance of a paper by Verwey on "Pentamethenylmalonic Acid and Pentamethenylacetic Acid," in a recent number of the *Berichte* (xxix., 1896) has led us to take the earliest opportunity of making known the results of some experiments which were commenced last spring, and which were undertaken, partly with the object

of synthesising dimethylhexamethenylmalonic acid and dimethylhexamethenylacetic acid—homologues respectively of the compounds derived by Verwey—and partly with the object of making a general study of hexamethylene derivatives.

To obtain these substances it was necessary to prepare dimethylketohexamethylene (*Trans.*, 1895, 349), and for this purpose a large quantity of dimethylpimelic acid was required; in the first place, therefore, we endeavoured to find a better method for preparing this acid than the one previously adopted (*Trans.*, 1891, 569), and this we accomplish in the following manner:—The acetyl-dimethylcaproic acid which is formed, together with dimethylpimelic acid, by the hydrolysis of ethylic dimethyldiacetylpimelate (*loc. cit.*) is dissolved in excess of aqueous sodium hydroxide and bromine is then added, in small quantities at a time, until bromoform is no longer produced; under these conditions the acetyldimethylcaproic acid seems to be converted quantitatively into dimethylpimelic acid.

This fact being established, the crude mixture of acids directly obtained from ethylic dimethyldiacetylpimelate may be submitted to oxidation in the above manner, the troublesome separation of the two acids thus being avoided.

Having prepared a considerable quantity of dimethylpimelic acid in this way, we converted it into dimethylketohexamethylene by distilling its barium salt and reduced the ketone with sodium in moist ethereal solution thus obtaining the corresponding alcohol, which has been recently described by Zelinsky; this alcohol was then converted into dimethylhexamethylene bromide by treating it with hydrobromic acid.

We then began to study the conditions under which ethylic dimethylhexamethenylmalonate could be prepared by the interaction of dimethylhexamethylene bromide and ethylic sodiomalonate, but the experiments were interrupted by the summer vacation, and have not yet been resumed; as, however, they will be continued at an early date the publication of this note seemed desirable.

The fact that Noyes (*Ber.*, 1896, 2326) has lately obtained from dihydrocampholytic acid (*cis*) a ketone which may be identical with dimethylketohexamethylene, enhances the interest which is attached to the further study of this compound.

(To be continued).

PHYSICAL SOCIETY.

Special General Meeting, November 27th, 1896.

Captain ABNEY, President, in the Chair.

THE Resolutions passed at the Special General Meeting held on October 30th were confirmed.

Ordinary Meeting.

Prof. RÜCKER, Vice-President, in the Chair.

The President (Captain ABNEY) described and exhibited some Apparatus for giving Diagrams of the Efficiency of a Photographic Shutter.

In addition to the "speed" of a shutter, which is concerned with the interval (T) between the moments when the shutter admits the first and last rays of light, it is most important to know the efficiency of the shutter. The efficiency may be defined as follows:—Let x represent the portion of the available aperture of the lens exposed by the shutter at a time t , and let X be the total available aperture. Then, if the shutter were perfectly efficient, *i.e.*, if the whole of the aperture were efficient during the time T , the quantity of light admitted would be proportional to XT . In other cases the quantity of light admitted will be proportional to—

$$\int_0^T x dt.$$

Hence the efficiency is—

$$\frac{\int_0^T x dt}{XT}.$$

The apparatus employed by the author consists of a slit placed near the shutter, so that the length of the slit is at right angles to the direction of motion of the shutter, and a lens, by means of which an image of the slit is thrown on to a rotating drum or plate. The slit, when the shutter is open, is illuminated by the light of an arc lamp; a condensing lens being employed. In order to obtain a time scale two devices have been employed. In one of these a spoked wheel is rotated at a known speed, so that each spoke, as it passes, momentarily cuts off the light. In the other arrangement a small lens, attached to the prong of a tuning-fork, throws a small spot of light on to the rotating drum, and thus gives a wavy line. Bromide paper or celloidin films are employed to record the diagrams.

If the shutter were perfectly efficient the diagram would consist of a rectangle, crossed, if the rotating wheel is used, by a number of white lines, caused by the interruption of the light by the spokes of the wheel. These lines give a time scale by which the speed of the shutter can be calculated.

The author showed a number of diagrams taken by the apparatus, and illustrating the behaviour of different shutters under varying conditions. In one of these the rebound of the shutter at quick speeds is clearly shown by each of the principal diagrams being followed by a small auxiliary one.

Prof. PERRY said he supposed that what was required was some method of showing the motion of the shutters.

Mr. BOYS suggested that the efficiency might be defined as the ratio of the area of the actual diagram to that of the rectangle having as base the time between the commencement and end of the exposure.

Mr. INWARDS asked if the author had made any experiments to determine the amount of shake communicated to the camera by the motion of the shutter.

Prof. PERRY said what was required was an exceedingly light shutter that got up a great speed before it reached the aperture.

The Author, in his reply, said he had investigated the question of the shake due to the movement of the shutter. He considered that the amount of this shake depended upon the extent of the movement of the centre of gravity of the shutter. With a small stop the Thornton-Picard shutter fulfilled Prof. Perry's requirements. The experiments have shown that the exposure does not always vary as the square of the aperture, on account of the small efficiency of some shutters for oblique rays. Thus in one case by doubling the aperture you only increase the light threefold.

The Society then adjourned till December 11th.

NOTICES OF BOOKS.

Hygienic Review of Chile. Vol. ii., No. 6. ("Revista Chilena de Higiene").

THE issue before us contains a paper on the bacteriological analysis of atmospheric dust, by Dr. Mamak Cádiz,—a summary of opinions in favour of and hostile to the Vitacuna water supplied to Santiago, from which we quote merely the damnable fact that it contains, per 1000 grms., 866 m.grms. of lead; and a series of clinical

observations on serotherapy, as applied in the treatment of cancer.

A Junior Course of Practical Chemistry. By FRANCIS JONES, F.R.S.E., F.C.S., Chemical Master in the Grammar School, Manchester. With a Preface by Sir H. E. Roscoe, F.R.S. London and New York: The Macmillan Co. (Ltd.). 1896.

THIS work is now in its eighth edition, and calls for little comment. Its teachings are correct, like those of very many other chemical manuals. It is arranged to suit the new Syllabus of the Science and Art Department, and is fitted up with an Appendix of questions and exercises.

CORRESPONDENCE.

COTTON SEEDS.

To the Editor of the Chemical News.

SIR,—Will you permit me to add a word to the letter of Dr. George F. Payne, published in the *CHEMICAL NEWS* of October 16th (lxxiv., p. 196).

It is rather curious that Dr. Blyth should not have been acquainted with the nature of the poisonous bases which are present sometimes in cotton seeds. The poisonous nature of these bases was first pointed out by Böhm in 1881, who discovered cholin in cotton seed. The presence of betain in the same substance was pointed out by Ritt-hausen and Weger in 1882. The fact that cholin was more poisonous than betain was subsequently determined by physiological experiments conducted by Gaetgens. A thorough study of these nitrogenous bases in cotton seeds has been made in this laboratory by Maxwell and the results published in the *American Chemical Journal*, vol. xiii., p. 469. In the third volume of my work on the "Principles and Practice of Agricultural Analysis," p. 429, occur the following sentences:—

"These bodies (viz., cholin, betain) have acquired an economic interest on account of their occurrence in cotton seed meal, which is so extensively used as a cattle food. It is evident from the relative proportions in which they occur that the less noxious base, betain, is the more abundant. It is possible, however, that the base originally formed is cholin and that betain is a secondary product. Experience has shown that it is not safe to feed cotton seed meal to very young animals, while moderate rations thereof may be given to full-grown animals without much expectation of deleterious results. In the case of toxic effects it is fair to presume that a meal has been fed in which the cholin is relatively more abundant than the betain."

The methods used in this laboratory for detecting, isolating, and separating the two bases are fully described on pp. 428-29 of the work referred to.—I am, &c.,

H. W. WILEY,
Chief of Division.

United States Department of Agriculture,
Div. of Chemistry, Washington, D.C.,
November 16, 1896.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 19, November 9, 1896.

M. Berthelot presented to the Academy a work which he has just published under the title "Science and Morals."

It contains various articles and discourses on the general part played by Science in Society and Education. It contains also biographical notices of Pasteur, Cl. Bernard, and P. Bert, and articles on the History of the Sciences, e.g., on the discovery of alcohol, on the preservation of ancient industries, on the chemistry of the Arabs, &c.

Composition of the Fruits of Phoenix melanocarpa.—Aimé Girard.—This fruit is a species or variety of date. Its saccharine matter consists entirely of levulose. It contains neither acids nor tannic matters, but abounds in pectine.

Action of Aluminium Chloride upon Camphoric Anhydride.—G. Blanc.—Not suitable for abstraction.

On the Essential Oil of Resin.—Eugene Charabot and G. Chiris.—The rotatory power of French oils is stronger than that of Turkish samples.

New Ferment in the Blood.—M. Hanriot.—This ferment, which the author names lipase, is very stable and acts principally upon fatty matters.

Chemical Method of Appreciating the Value of Wheat Flours from the Baker's point of view.—E. Fleurent.—The author finds that gluten may be divided into three classes:—1. Glutens which are decidedly elastic; 2. Drier and more brittle glutens, easily desiccated and more frangible; 3. Very tender glutens, easily elongated but scantily elastic. These differences are due to the different proportions of glutenine and gliadine in the glutens examined.

Application of the Röntgen Rays in Palæontology.—M. Lemoine.—The author finds that the X rays easily traverse the fossilised walls of bony pieces, apparently very opaque. This method will in many cases be an improvement on the use of sections.

Zeitschrift für Analytische Chemie.
Vol. xxxv., Parts 4 and 5.

Reactions for Glucose, Aldehyds, and Ketones.—A. Jaworowski (*Pharm. Post and Pharm. Central Halle*).—Orthonitrophenol, like picric acid, if heated with an alkaline solution of glucose, produces a brown colouration. Commercial nitrobenzol, under similar conditions, colours a solution of glucose at first red and then a dirty brown. If 3 c.c. of dilute sulphuric acid are mixed with 0.1 grm. of sodium vanadate, and then superstratified with solution of glucose, there appears a green or blue ring. If solution of glucose is boiled with a little iodic acid and soda lye, the liquid acidulated when cold, and superstratified with ammonia, there is formed a dark precipitate (nitrogen iodide). If solution of glucose is heated with Jaworowski's ammonia test (1 part mercuric chloride, 1 part sodium carbonate, 4 parts sodium chloride, 30 parts water), there is formed a yellow precipitate, afterwards turning grey. A similar reaction occurs with the Nessler test (the precipitate being at first reddish brown, then brown, dirty green, and at last grey). All these reactions hold good for the aldehyds and ketones, excepting the iodic acid reaction.

A Boiling Flask, consisting in its lower part of milk-glass, is proposed by H. M. Smith (*CHEMICAL NEWS*) for determining sugar with Pavy's solution.

An Electric Blowpipe.—H. N. Warren (*CHEMICAL NEWS*).

Determination of the Halogens.—A series of notes from different authorities.

Behaviour of Tartaric Acid and its Alkaline Salts with certain Agents.—Magnier de la Source (*Comptes Rendus*).

Reactions of Formal Aldehyd.—T. H. Lee.—(From the *CHEMICAL NEWS*).

MISCELLANEOUS.

Forthcoming Books.—We learn from Mr. Hart, of the Chemical Publishing Co., Lafayette Press, Easton, Pennsylvania, that they will shortly bring out an important chemical work by Dr. Wiley in three volumes, and one by T. S. Stillman on Engineering Chemistry. Our readers may be interested in knowing that the staff at Mr. Hart's office consists entirely of chemists, thereby helping to approach the ideal in publishing chemical books.

The Royal Society.—The following Officers and Members of Council were elected November 30, 1896:—

President.—Sir Joseph Lister, Bart., F.R.C.S., D.C.L.

Treasurer.—Sir John Evans, K.C.B., D.C.L., LL.D.

Secretaries.—Prof. Michael Foster, M.A., M.D., D.C.L., LL.D.; Prof. Arthur William Rücker, M.A., D.Sc.

Foreign Secretary.—Edward Frankland, D.C.L., LL.D.

Other Members of the Council.—Prof. William Grylls Adams, M.A.; Prof. Thomas Clifford Allbutt, M.D.; Prof. Robert Bellamy Clifton, M.A.; William Turner Threlton Dyer, C.M.G.; Prof. James Alfred Ewing, M.A.; Lazarus Fletcher, M.A.; Walter Holbrook Gaskell, M.D.; Prof. Alfred George Greenhill, M.A.; William Huggins, D.C.L.; Prof. Charles Lapworth, LL.D.; Major Percy Alexander MacMahon, R.A.; Prof. Raphael Meldola, F.C.S.; Prof. William Ramsay, Ph.D.; The Lord Walsingham, M.A.; Prof. Walter Frank Raphael Weldon, M.A.; Admiral William James Lloyd Wharton, C.B.

MEETINGS FOR THE WEEK.

MONDAY, 7th.—Society of Arts, 8. "The Use of Gas for Domestic Lighting" (Cantor Lectures), by Prof. Vivian B. Lewes.

Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. "The Alkali Manufacture—An Historical Sketch," by Alfred E. Fletcher. "Notes on the Spontaneous Oxidation of Aluminium in contact with Mercury," by H. F. Hunt and L. J. Steele.

WEDNESDAY, 9th.—Society of Arts, 8. "Mining at Great Depths," by Bennett H. Brough, Assoc. R.S.M.

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JOHN PHILLIPS, Secretary.

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THE CHEMICAL NEWS.

VOL. LXXIV., No. 1932.

THE ANALYSIS OF "CAP COMPOSITION."

By F. W. JONES and F. A. WILLCOX, B.Sc.

"CAP composition" usually consists of the ingredients potassium chlorate, antimony sulphide, and mercury fulminate, and to estimate these substances in the presence of each other by ordinary analytical methods is a difficult process, since the separation of antimony sulphide and mercury fulminate in the presence of potassium chlorate necessitates the treatment of the mixture with hydrochloric acid, and this produces an evolution of sulphuretted hydrogen from the sulphide, and a consequent precipitation of sulphur; and potassium chlorate cannot be separated from the other ingredients by treatment with water, owing to the appreciable solubility of mercury fulminate in cold water.

We observed in the course of some experiments on the solubility of mercury fulminate that this body was readily soluble in acetone and other ethereal solvents when they were saturated with ammonia gas, and that potassium chlorate and antimony sulphide were insoluble in pure acetone saturated with ammonia: and these observations at once afforded a simple method of separating the three ingredients of cap composition. By employing this solution of acetone and ammonia an analysis can be made in a comparatively short time, and yields results of sufficient accuracy for all technical purposes.

The following are the details of the analysis:—A tared filter-paper is placed in a funnel, to the neck of which has been fitted a piece of rubber tubing provided with a clip. The paper is moistened with the solution of acetone and ammonia; the cap composition is weighed off directly on to the filter-paper, and is then covered with the solution of acetone and ammonia, and allowed to stand for three or four hours. It is then washed repeatedly with the same solution until the washings give no colouration with ammonium sulphide, and afterwards washed with acetone until the washings give no residue on evaporation, dried, and weighed.

The paper is again put in the funnel, and washed with water until free from potassium chlorate, dried, and weighed.

If c = weight of composition taken,

d = weight of filter-paper,

a = weight after first extraction,

b = weight after second extraction;

then $c + d - a$ = weight of fulminate of mercury,

$c + d - a - b$ = weight of potassium chlorate,

$b - d$ = weight of antimony sulphide.

The results of the analyses, by this method, of two mixtures of known composition are given below:—

	A.		B.	
	Percentage taken.	Percentage found.	Percentage taken.	Percentage found.
Antimony sulphide	36.47	36.25	37.34	37.22
Potassium chlorate	33.25	33.71	46.03	46.43
Mercury fulminate	30.27	30.02	16.61	16.34

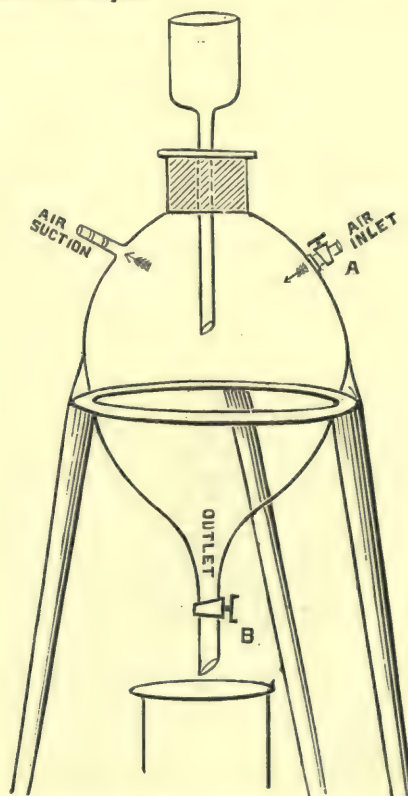
It is necessary, in carrying out an analysis, to previously grind the composition in an agate mortar (of course with due care, and taking only small quantities at a time), and to dry the filter-paper always at the same temperature.

FILTER FLASK.

By W. DIAMOND.

I HAVE enclosed a rough drawing of what I think a decided improvement on the filter-pump flask in general use. The shape and use of the ordinary one we all know. My improvement is as follows:—

Instead of the flask being flat-bottomed I have it made dome-shaped, at the bottom of which there is a tap, B, which acts as an outlet. Close to the neck there is another tap, A, but a very small one, which breaks the vacuum when turned on. The whole is supported upon a tripod, the flask having tabs projecting which rest upon the rim of the tripod.



This apparatus saves a lot of unnecessary work. If a chemist or a student has a large volume of liquid to filter, perhaps he may have to detach the cork and funnel from the neck several times in course of filtration, which also incurs the possibility of losing a portion of the precipitate or residue from the filter by jarring. These difficulties are somewhat alleviated by my apparatus. To dispense with the filtrate the air-tap, A, is turned on, thus allowing a current of air to get into the flask and breaking the vacuum; then the outlet-tap, B, may be turned on, and so run the liquid away; when empty turn the taps off, and all is again working.

Chemical Works Laboratory, Pye Bridge,
November 24, 1896.

Reactions of Gallic Acid, Tannin, Pyrocatechin, and Protocatechuic Acid. — F. Koch (*Archiv der Pharmacie*).—The reagents are solutions of ferric chloride at $\frac{1}{2}$, 1, 2, and 4 per cent, and $\frac{1}{2}$ per cent solution of sodium bicarbonate. A drop of the solution of ferric chloride is first added and then the sodium bicarbonate solution is added drop by drop until the full colour is produced.

IODOMETRIC DETERMINATION OF SELENIOS AND SELENIC ACIDS.*

By JAMES F. NORRIS and HENRY FAY.

THE methods already in use for the volumetric determination of selenious acids are those of Muthmann and Schaefer (*Ber. d. Chem. Ges.*, xxvi., 1008), and Gooch and Peirce (*Am. J. Sci.*, i. [4], 31). The former method has been studied by Gooch and Reynolds (*Ibid.*, xxx., 254), and found to be inaccurate. The method of Gooch and Peirce depends upon the reduction of a known weight of potassium iodide in sulphuric acid solution by selenious acid in presence of arsenic acid. The difference between the arsenious acid equivalent to the potassium iodide and the amount found, is a measure of the selenious acid. Selenic acid is first reduced by boiling with potassium bromide and sulphuric acid under definite conditions.

The method here proposed requires fewer reagents, occupies less time, and gives more accurate results. The determination depends on the reaction between sodium thiosulphate and selenious acid in presence of hydrochloric acid. So far we are unable to state the complete reaction which takes place, but have found that 1 molecule of selenious acid is exactly equivalent to 4 molecules of sodium thiosulphate. After standing about twenty-four hours, part of the selenium is precipitated. In neutral solution the reaction takes place slowly, and is not complete after standing a day. In a strong neutral solution there is immediate precipitation of selenium, and the reaction becomes strongly alkaline. In this solution no sulphates were found. It is proposed to make a more complete study of this reaction.

The reagents used were carefully purified. Re sublimed iodine was sublimed from one-third of its weight of potassium iodide, and dissolved in potassium iodide free from iodate. This precaution was necessary, as the titrations were made in acid solution. A hot concentrated solution of potassium iodide was boiled five minutes with the addition of a small quantity of hydrochloric acid, the solution cooled rapidly, and the precipitate washed with alcohol to remove free iodine. The potassium iodide gave no reaction with starch when acidified with hydrochloric acid.

As the commercial sodium thiosulphate gave a different iodine-value in acid and neutral solution, it was found necessary to re-crystallise it to remove the sulphite, although the presence of the latter was not indicated by barium chloride. The sodium thiosulphate was standardised against re-sublimed iodine and pure sodium arsenite,

The selenious acid was prepared from commercial selenium by evaporating to dryness with concentrated nitric acid. The selenium dioxide thus obtained was reduced by sodium sulphite and hydrochloric acid, and the pure selenium was again oxidised by evaporating to dryness with nitric acid, and the residue re-sublimed. In order to prevent reduction the oxide was sublimed in a small beaker, covered with a watch-glass, and containing a drop of strong nitric acid. By this method long, perfectly white, needles of selenium dioxide can be obtained which are free from selenic acid. About 2 grms. were weighed accurately, dissolved in water, and diluted to 500 c.c.

The selenic acid was prepared by dissolving about 2 grms. of selenium dioxide in 200 c.c. of water, and adding a strong solution of potassium permanganate until a permanent pink colour remained after heating one-half hour at 60°C. Sulphurous acid was then added until only a small amount of manganese dioxide remained, and the solution filtered and diluted to 500 c.c. Sodium thiosulphate titrated in the presence of a definite portion of this solution, acidified with hydrochloric acid,

gave the same iodine-value as without its presence, thus showing the absence of selenious acid.

The flasks and burettes were calibrated according to the method of Morse and Blalock (*Amer. Chem. Journ.*, xvi., 479).

Determination of Selenious Acid.

A definite portion of selenious acid was measured off, diluted with ice-water and 10 c.c. hydrochloric acid (1·12 sp. gr.). An excess of one-tenth normal solution of sodium thiosulphate was added and titrated back with iodine solution. One molecule selenious acid, SeO_2 , is equivalent to 4 molecules of thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. It was found necessary to have enough hydrochloric acid present to set free all of the thiosulphuric acid. If the solution is cold, a large excess of hydrochloric acid does not affect the titration. The following is a series of eight consecutive determinations:—

SeO_2 taken.	SeO_2 found.	SeO_2 taken.	SeO_2 found.
0·0829	0·0829	0·1366	0·1367
0·0829	0·0829	0·1366	0·1368
0·1242	0·1242	0·1656	0·1659
0·1242	0·1242	0·2070	0·2071

It will be seen that the error varies from 0·00 to 0·18 per cent, the average being 0·06 per cent. The method is therefore one of the most accurate of iodometric methods and can be used conveniently for the standardisation of sodium thiosulphate. The solution of selenious acid is entirely stable.

Determination of Selenic Acid.

As selenic acid does not react with sodium thiosulphate, it is first reduced by boiling with hydrochloric acid and titrated as above. It was found necessary to modify the method of Gooch and Evans (*Am. J. Sci.*, l., 400) for the reduction by hydrochloric acid, as there was invariably loss of selenium.

To a measured portion of selenic acid is added 25 c.c. concentrated hydrochloric acid, and the solution diluted to 100 c.c. The solution is boiled for one hour, precaution being taken not to allow the volume to go below 75 c.c., cooled, diluted with ice-water, and the selenious acid determined by titration. The following results were obtained consecutively:—

SeO_2 taken.	SeO_2 found.	SeO_2 taken.	SeO_2 found.
0·1011	0·1009	0·1598	0·1595
0·1011	0·1008	0·1598	0·1595
0·1067	0·1067	0·2023	0·2024
0·1067	0·1065	0·2665	0·2662

Determination of a Mixture of Selenious and Selenic Acids.

Two portions of a solution containing a known quantity of selenious and selenic acids were measured off. In one the selenious acid was determined by direct titration; in the other the total selenium, after reduction of the selenic acid, was determined. On heating the solution in the reduction of selenic acid, some selenium is precipitated, which goes into solution when the chlorine is evolved. The method was tested by the following determinations:—

SeO_2 taken.	SeO_2 found.	SeO_2 taken.	SeO_2 found.
0·0467	0·0467	0·1013	0·1015
0·0467	0·0466	0·1013	0·1016
0·0934	0·0933	0·0506	0·0504
0·1868	0·1865	0·1012	0·1015

—*American Chemical Journal*, xviii., No. 8.

Directorship of the Observatory of Paris. — At a recent meeting of the Académie des Sciences M. Loewy was recommended to the Minister of Public Instruction for this appointment.

* Contributions from the Chemical Laboratory of Massachusetts Institute of Technology.

THE NEUTRALITY OF SALTS AND COLOURED INDICATORS.

By H. LESCŒUR.

CHEMISTS formerly defined bases by their property of turning the syrup of violets green, of reddening turmeric paper, and of turning red litmus to a blue; whilst acids were characterised by their property of reddening blue litmus. On mixing acids and bases so as to neutralise their action on the coloured indicators, they obtained the *mon* or *neutral* salts—combinations of acid and of base which can neither redden blue litmus nor turn red litmus blue,—and this definition has continued to the present day.

This manner of defining the neutrality of salts has given rise to objections. Certain salts, *e.g.*, zinc sulphate, redden litmus. They are therefore not neutral according to the definition, whilst their analogies do not allow us to separate them from the salts which are truly neutral, *e.g.*, sodium sulphate. Berzelius therefore proposed, whilst retaining for the salts of potassium and sodium the signs of neutrality afforded by coloured indicators, to take no account of this character for the other metallic salts, and to agree for the nomenclature to be guided by the analogy of the corresponding sodium salts. Thus the neutral sulphates will be those which, like neutral sodium sulphate, contain three times more oxygen in the acid than in the base.

In reality at the root of this question there lies a misunderstanding on the interpretation of the indications given by litmus—a misunderstanding which prevails to this day.

Litmus contains a red colouring-matter, which forms blue compounds with alkalis. In pure water or in presence of an acid this indicator will be red. It will be blue in presence of a free alkali. In presence of an insoluble base it sometimes remains red without modification, as in the case of alumina; sometimes it gives violet compounds, insoluble or slightly soluble, more or less decomposable by water, and the solution will be more or less completely decolourised whilst ordinarily remaining rose.

If, into a solution containing an insoluble base and a mineral acid in excess, we pour an alkali in presence of litmus so as to change the medium from acidity to alkalinity, the litmus varies from red to blue, and this change is sometimes sufficiently distinct to afford a means of determination, as is the case with the salts of aluminium. But the change ensues not at the moment when the acid is saturated, and the precipitation of the acid commences, but when the precipitation is completed, and the medium contains alkali in excess.

For most of the metals the change is most obscure, and between the moment where there is still free acid and when the alkali is in excess, *i.e.*, during the period of precipitation, the litmus passes through all the intermediate shades between red and blue.

It is rational to regard as neutral the state of the medium during the course of precipitation. It then contains neither free acid nor free alkali. The case of alum and the analogous salts seems to show that the red colouration of litmus does not necessarily indicate the acidity of the medium. It may just as well signify neutrality. The different phenomena presented by other metallic salts as regards their variations and their obscurity cannot prevail against this opinion.

This interpretation is confirmed by the study of the other indicators, which are now very numerous.

Phenolphthalein is a colourless substance yielding red compounds with the alkalis. It does not combine with the insoluble metallic oxides. If into a medium containing an insoluble base, and an acid in excess, we pour an alkali in presence of phthaleine the solution will be at first colourless owing to the presence of free acid; when this is neutralised, and oxide is precipitating, it still remains colourless, and the change to redness does

not take place until all the oxide being thrown down the medium contains alkali in excess.

Phthaleine by its change of colour indicates not the passage from acidity to alkalinity, but the passage from neutrality to alkalinity. Its indications are comparable to those of litmus, but are infinitely more decided.

Helianthine (Poirrier's orange No. 3) is a substance sensibly colourless in an alkaline or neutral medium, but turning red in presence of free acids. If into the solution of a metallic oxide in excess of acid we pour an alkali in presence of helianthine, the medium takes at first a rose colour; then the change to yellow takes place when all the free acid is saturated. The precipitation takes place only then. This indicator signifies therefore the passage from acidity to neutrality. The data which it yields are absolutely opposite to those of litmus and phthaleine.

Conclusion.—If we combine the data of these two orders of colouring matters the notion of neutrality takes a character of great distinctness. The red colouration of phthaleine, or the blueness of litmus indicating the presence of free alkali, and the rose colouration of helianthine indicating the presence of a free acid, we shall reserve the term *neutral*, for the state of a medium such that on the one part helianthine remains colourless, and on the other part phthaleine remains colourless and litmus red.

We thus recognise that salts such as alum, zinc sulphate, &c., which Berzelius considered acid to litmus, are in reality neutral to coloured reagents, and that in the question of the neutrality of salts there is agreement between theory and the data of coloured indicators.—*Comptes Rendus*, cxxiii., p. 811.

COLOUR PHOTOGRAPHY.*

By Professor G. LIPPMANN, Membre de l'Institut (France),

(Concluded from p. 276).

How are we now to prove that the above theory is really applicable to the colour photograph you have seen? How can we demonstrate that those bright colours are due not to pigments, but to the interference, as in the case of soap-bubbles? We have several ways of proving it.

First of all, we are not bound to the use of a peculiar chemical substance, such as Becquerel's subchloride of silver; we obtain colour with a variety of chemicals. We can, for instance, dispense entirely with the use of a silver salt; a film of gelatin or coagulated albumen impregnated with bichromate of potash, then washed with pure water after exposure, gives a very brilliant image of the spectrum.

Secondly, the colours on the plate are visible only in the direction of specular reflection. The position of the source by which we illumine the photograph being given, we have to put the eye in a corresponding position, so as to catch the regularly reflected rays. In every other position we see nothing but a colourless negative. Now, as you are aware, the colours of pigments are seen in any direction. By projecting again a photograph of the spectrum, and turning it to and fro, I can show you that the colours are visible only in one direction.

Thirdly, if we change the incidence of the illuminating rays,—that is, if we look at the plate first in a normal direction, then more and more slantingly,—we find that the colours change with the incidence exactly as they do in the case of soap-bubbles or of Newton's rings; they change according to the same law and for the same reasons. The red end of the spectrum turns successively to orange, yellow, green, blue, and violet. The whole system of colours, the image of the spectrum, is seen to move down into the part impressed by the infra-red.

* A Lecture delivered at the Royal Institution of Great Britain, April 17, 1896.

This is what we expect to happen with interference colours, and what again we cannot obtain with pigments.

Fourthly, if while looking at the film normally, we suffer it to absorb moisture,—this can be done by breathing repeatedly on its surface,—we see that the colours again change, but in an order opposite to that above described. Here the blue end of the spectrum is seen to turn gradually green, yellow, orange, red, and finally infra-red—that is, invisible. The spectrum this time seems to move up into the ultra-violet part of the improved film. By suffering the water to evaporate, the whole image moves back into its proper place. This experiment may be repeated any number of times.

The same phenomenon may be obtained with Newton's apparatus, by slowly lifting the lens out of contact with the plane surface. The explanation is the same in both cases. The gelatin swells up when imbibing moisture. If we consider, for instance, the violet of the spectrum, the small intervals between the strata corresponding to violet rays, gradually swell up to the values proper for green, and for red, and for infra-red; green, then red, then infra-red, are therefore successively reflected.

We will wet this photograph of the spectrum with water, project it on the screen, and watch the colours coming back in the order prescribed by theory.

It is necessary to use a transparent film, since an opaque one, such as is commonly in use, would hide the mirror from view; the sensitive substance must be grainless, or at least the grains must be much finer than the dimensions of the strata they are intended to form, and therefore wholly invisible. The preparation of transparent layers gave me at first much trouble; I despaired for years to find a proper method for making them. The method, however, is simply this:—If the sensitive substance (the silver bromide, for instance) be formed in presence of a sufficient quantity of organic matter, such as albumen, gelatin, or collodion, it does not appear as a precipitate; it remains invisible; it is formed, but seems to remain dissolved in the organic substratum. If, for instance, we prepare a film of albumen-iodide in the usual way, only taking care to lessen the proportions of iodide to $\frac{1}{4}$ per cent of the albumen, we get a perfectly transparent plate, adapted to colour photography.

We want now to go a step further. It is very well for physicists to be contented with working on the spectrum, since that contains the elements of every compound colour; but we all desire to be able to photograph other objects than the spectrum—common objects with the most compound colours. We have again but to take theory as a guide, and that tells us that the same process is able to give us either simple or compound colours. We have then to take a transparent and correctly isochromatised film, exposing it with its mercury backing, then develop and fix it in the usual way; the plate, after drying, gives a correct coloured image of the objects placed before the camera. Only one exposure, only one operation is necessary for getting an image with every colour complete.

A plausible objection was offered at first to the possibility of photographing a mixture of simple colours. The objection was this: a ray of violet gives rise to a set of strata separated by a given interval; red light produces another set of strata with another interval; if both co-exist, the strata formed by the red are sure to block out here and there the intervals left between the strata formed by the violet. Is it not to be feared that one fabric will be blurred out by the other, and the whole effect marred? The confusion would be still worse if we consider the action of white light, which contains an infinity of simple components; every interval here is sure to be blocked up.

Mathematical analysis, however, shows this objection to be unfounded; we have great complexity, but not confusion. Every compound ray, both coloured and white, is faithfully rendered. As an experimental proof of this, we will project on the screen photographs of very different objects, namely, stained glass windows,

landscapes from Nature, a portrait made from life, and vases and flowers.

That the colours here observed are due to interference, and not to the presence of pigments, can be shown in the same way as with the spectrum. Here, again, we observe that the colours are visible only in the direction of specular reflection, that they change with the angle of incidence, that they change and disappear by wetting, and re-appear by drying. Pigments remain equally visible and unaltered in colour under every incidence. If we attempted to touch up one of our photographs with oil or water-colours, the adulterated place would stand out on a colourless background by merely observing by diffused light. It is therefore impossible either to imitate or touch up a colour photograph made by the above-described interferential method.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 5th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 280).

142. "*Sulphocamphylic Acid* ($C_9H_{14}SO_5$), with Remarks on the Constitution of Camphoric Acid and of Camphoronic Acid." By WILLIAM HENRY PERKIN, jun.

In two previous notices (*Proc.*, 1893, 109; 1895, 23), the author stated that when sulphocamphylic acid is fused with potash, the principal products of the reaction are two isomeric acids, $C_9H_{12}O_2$ (or $C_8H_{11}COOH$), for which he proposes the names *α-camphylic acid* and *β-camphylic acid*; the former melts at 148° , the latter at about 105° .

Besides these two acids, it has since been found that *αα-dimethylsuccinic acid*, $COOH \cdot C(CH_3)_2 \cdot CH_2 \cdot COOH$, and small quantities of *dicamphylic acid*, $C_{16}H_{22}(COOH)_2$ (m. p. 225°) are formed during the fusion. The latter acid, which has not been very fully investigated, is decomposed on distillation, with formation of *α-camphylic acid*.

α-Camphylic acid (m. p. 148°) is readily acted on by phosphorus trichloride, with formation of *α-camphylic chloride*, $C_8H_{11}COCl$ (b. p. about $138-140^\circ$ at 60 m.m., with decomposition). The *anilide*, $C_8H_{11}CONHC_6H_5$, melts at 111° , and the *ethyl salt*, $C_8H_{11}COOC_2H_5$, is a colourless oil, which distils at 132° (70 m.m.).

All these derivatives yield *α-camphylic acid* again on hydrolysis, and not an isomeric acid (see below under *β-camphylic acid*).

α-Camphylic acid dibromide, $C_8H_{11}Br_2COOH$, is formed when bromine is added to the solution of *α-camphylic acid* in chloroform; it melts at 157° , and when digested with glacial acetic acid it is converted into *bromo-α-camphylic acid*, $C_8H_{10}BrCOOH$ (m. p. 107°), with elimination of hydrogen bromide.

α-Camphylic acid dihydrobromide, $C_8H_{13}Br_2COOH$, is produced by dissolving *α-camphylic acid* in a saturated solution of hydrogen bromide in glacial acetic acid. It melts at $156-157^\circ$, and when boiled with water or digested with quinoline it is re-converted into *α-camphylic acid*.

On reduction with sodium amalgam, *α-camphylic acid* yields *dihydro-α-camphylic acid*, $C_8H_{13}COOH$, a colourless oil, which distils at $165-170^\circ$ (50 m.m.); it is an unsaturated acid, and possibly identical with the dihydro-acid obtained from *β-camphylic acid* by reduction (see below). When oxidised with potassium permanganate *α-camphylic acid* is converted into a new monobasic acid of the formula $C_8H_{13}O_3COOH$ (m. p. 148°), and this acid, on oxidation with chromic acid, is decomposed, with formation of acetone, acetic acid, and other products which are at present under investigation.

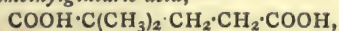
β -Camphylic acid, $C_8H_{11}COOH$ (m. p. 105°), combines readily with bromine yielding β -camphylic acid dibromide, $C_8H_{11}Br_2COOH$ (m. p. about 177°), and this acid, when heated with glacial acetic acid, loses 1 mol. of hydrogen bromide with formation of bromo- β -camphylic acid, $C_8H_{10}BrCOOH$ (m. p. 150°), in which the bromine atom is so firmly bound that the acid may be boiled with strong potash, or with zinc dust and acetic acid, for some time without decomposition. When digested with quinoline, there is no elimination of hydrogen bromide, but the acid is converted into $C_8H_{10}BrCOOH$, isobromo- β -camphylic acid (m. p. 168°); probably these two bromo- β -camphylic acids are stereoisomeric.

β -Camphylic acid hydrobromide, $C_8H_{12}BrCOOH$, is produced when β -camphylic acid is dissolved in a fuming solution of hydrogen bromide in glacial acetic acid. It melts at $138-140^\circ$, and, when boiled with water or digested with quinoline, is re-converted into β -camphylic acid.

When treated with sodium amalgam, β -camphylic acid yields an oily reduction product, $C_8H_{13}COOH$, which boils constantly at 190° (80 m.m.); this oil is probably a mixture of isomeric dihydro camphylic acids; as, under certain conditions, it deposits crystals of a dihydrocamphylic acid which melts at 130° .

Iso- β -camphylic acid, $C_8H_{11}COOH$, is formed when β -camphylic acid is digested with phosphorous tri-chloride and the product, after fractionation, decomposed with water. It melts at 130° , and is probably stereoisomeric with β -camphylic acid; the chloride, $C_8H_{11}COCl$, distills with very little decomposition at 135° (60 m.m.); the ethyl salt, $C_8H_{11}COOC_2H_5$, is a colourless oil which boils at 140° (60 m.m.), and the anilide, $C_8H_{11}CONHC_6H_5$, crystallises in colourless needles and melts at 103° .

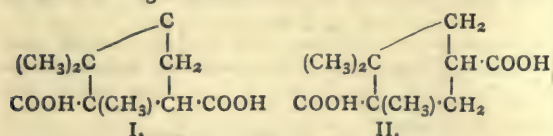
When oxidised, first with potassium permanganate and then with chromic acid, β -camphylic acid yields α -dimethylsuccinic acid, $COOH \cdot C(CH_3)_2 \cdot CH_2 \cdot COOH$ (m. p. 140°), α -dimethylglutaric acid,—



and a ketonic acid, $C_8H_{11}O_3$, which melts at about $50-51^\circ$.

This latter acid gives a beautifully crystalline semicarbazone, $C_9H_{17}N_3O_3$ (m. p. 187°); on oxidation with nitric acid, it yields α -dimethylsuccinic acid, and, when treated with bromine and potash, it is decomposed, with formation of tetrabromomethane and α -dimethylglutaric acid; it is therefore exceedingly probable that it is of the formula $CH_3 \cdot CO \cdot C(CH_3)_2 \cdot CH_2 \cdot CH_2 \cdot COOH$, an acetyl-dimethylbutyric acid, and very likely identical with an acid, $C_9H_{11}O_3$, which Tiemann (*Ber.*, 1895, xxviii., 2176) obtained by the oxidation of β -dihydroxydihydrocampholenic acid with chromic acid, and to which he assigns the constitution given above.

The various decompositions of α - and β -camphylic acids, briefly stated above, as well as the results of a number of further experiments, which the author hopes soon to be able to communicate to the Society, throw much light on the constitution of these acids, as well as on the constitution of sulphocamphylic acid, and indirectly on that of camphoric acid. In this short abstract it is, of course, not possible to enter into this matter in detail, but it may be stated that it is exceedingly difficult to account for the observed behaviour of these substances on the assumption that the formulæ either of Bredt or of Tiemann for camphoric acid are correct. If, however, camphoric acid has the constitution represented by either of the following formulæ:—

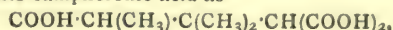


(of which the author considers formula I. the more prob-

able), then not only the formation of acetyldimethylbutyric acid from sulphocamphylic acid, but also the various decompositions of the camphylic acids, may be readily understood, and the author has further satisfied himself that all the other reactions of camphoric acid are at least as readily, and, in most cases much more easily, explained with the help of these formulæ than with that of any other formulæ which have, so far, been suggested. The author hopes that the discussion of these new formulæ will be reserved until he has been able to explain their application in the detailed description of the experimental results indicated above.

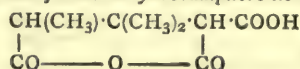
Camphoric Acid.—Bredt has assigned to this acid the formula $COOH \cdot CH_2 \cdot C(CH_3)_2 \cdot (COOH) \cdot CH_2 \cdot COOH$, and it seems very probable that this expression (which also follows from the formulæ I. and II. given above) is the correct one.

Tiemann (*Ber.*, 1895, xxviii., 1089), on the other hand, represents camphoric acid as—

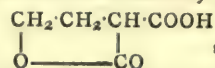


and when the paper putting forward this view appeared, the author privately suggested to Professor Tiemann that this expression could hardly be correct, since the acid, on heating, does not lose carbon dioxide, forming a corresponding dibasic acid, as would be the case if, as represented, the acid were a derivative of malonic acid.

Tiemann (*Ber.*, 1895, xxviii., 2163) replied to this that the acid did not decompose in this way, because it first loses water, and yields anhydrocamphoric acid,—



which he considers would be stable at high temperatures. But an acid of this formula is similarly constituted to—



carbobytyrolactonic acid, which, at 120° , very readily decomposes, with elimination of carbon dioxide and formation of butyrolactone.

In contact with water, anhydrocamphoric acid is at once converted into camphoric acid, and it appeared to the author that the validity of Tiemann's formula might be tested by heating an aqueous solution of camphoric acid at high temperatures. The result of experiments on this point showed that camphoric acid is not appreciably decomposed when heated with water in sealed tubes at $225-235^\circ$ for two hours, a result which appears to the author to prove conclusively that Tiemann's formula cannot be correct.

In confirmation of this it may be mentioned that Bredt (*Annalen*, ccxcii., 131) has lately shown that the triethylic salt of camphoric acid, which according to Tiemann should contain the group $-CH(COOC_2H_5)_2$, does not react with sodium.

143. "On Pettekofer's Method for Determining Carbonic Anhydride in Air." By Professor LETTS, D.Sc., Ph.D., and R. F. BLAKE, F.I.C.

The authors discuss the errors in the process of absorbing the carbonic anhydride from a sample of air collected in a glass vessel by baryta, and titrating with acid, and show that, in addition to the more obvious sources of error, the action of the alkaline absorbent on the glass is one of importance.

In order to avoid it they coat both the receiver containing the air sample and the bottle holding the stock of the standard solution of baryta with paraffin wax. By this means they at once obtained more concordant results in a series of determinations. They then proceeded to test the degree, both of accuracy and of delicacy, of Pettekofer's process if carried out with all the available precautions which suggested themselves. For this purpose they employed paraffined receiving vessels, an

apparatus for performing the titrations in a vacuum, and burettes of special construction. In addition, an apparatus was used for delivering, very accurately, measured volumes of pure carbonic anhydride into known volumes of air previously freed from that gas.

Experimenting with such mixtures of the two as occur in air, containing about 3 vols. carbonic anhydride in 10,000, the authors show that with careful work the mean error in the determinations need not exceed -0.04 part. The actual quantity of carbonic anhydride added to each receiver full of air, in a series of five experiments, amounted to 0.927 c.c.; the mean amount, found to be 0.916 c.c., giving, therefore, a mean error of -0.011 c.c.

They thus show that Pettenkofer's process, if suitably performed, is one of great accuracy and delicacy.

After giving the results of a series of determinations of carbonic anhydride in ordinary air, the authors comment on the method described by Messrs. Symons and Stephens (*Trans.*, 1896, 869) for such determinations and some of the results obtained by them. Sources of error in the process are pointed out, especially the introduction of small quantities of carbonic anhydride with the steam used to render the receiving vessels vacuous. In support of this contention they draw attention to the experiment described by Messrs. Symons and Stephens in which 0.2 c.c. of carbonic anhydride were thus found in a flask of 3 litres capacity, an amount corresponding with nearly 0.67 volumes in 10,000 supposing the flask to have been filled with air, which is nearly one-fifth the total quantity usually found in "fresh" air.

Although aware of the error thus introduced, Messrs. Symons and Stephens do not (as far as the authors can judge from their paper) make any correction for it in their subsequent determinations.

Ordinary Meeting, November 19th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

Mr. W. H. MERRETT was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. William Ross Innes, B.Sc., Ph.D., Mason College, Birmingham; Theophilus Henry Lee, Hampden House, Phenix Street, N.W.; Frank Southerden, 75, Barry Road, Dulwich, S.E.; Basil William Turner, Collins Street, Annandale, Sydney, N.S.W.

The certificates of the following Candidates, recommended by the Council under By-law I., par. 3, were also read:—

Gopal Chandra Bauerfee, Cawnpore, N.W.P.; Eric David Ewan, Port of Spain, Trinidad.

Of the following papers those marked * were read:—

*144. "Sulphocamphoric Acid and Derivatives of Camphorsulphonic Acid." By ARTHUR LAPWORTH, D.Sc., and FREDERIC STANLEY KIPPING, Ph.D., D.Sc.

The compounds obtained by treating α -bromocamphorsulphonic acid with nitric acid and with potassium permanganate respectively under various conditions, have been examined, and are described in this paper. The action of nitric acid, as stated in an earlier note (*Proc.*, 1896, xii., 77), gives rise to the formation of a hydroxy-dibromocamphorsulphonic acid of the composition $C_{10}H_{14}Br_2SO_5$, a sulpholactone of the composition $C_{10}H_{12}Br_2SO_4$, and a substance which was thought to be sulphocamphoric acid, but which was isolated only in the form of its ammonium dihydrogen salt.

An ammoniacal solution of potassium permanganate was found to be much more suitable than nitric acid for the oxidation of α -bromocamphorsulphonic acid, and with this reagent the principal product is sulphocamphoric acid, a simple substitution derivative of ordinary d -camphoric acid.

Sulphocamphoric acid, $SO_3H \cdot C_8H_{13}(COOH)_2$, crystallises from aqueous solution in large striated plates, which

contain water of crystallisation, and from ethylic acetate in beautiful, transparent, pyramidal crystals which effloresce on exposure to the air; the anhydrous acid melts at 188° , at which temperature it is probably converted into its anhydride. It is very readily soluble in water, alcohol, acetic acid, and acetone, and has all the ordinary properties of sulphonic acids; several of its salts are described.

Sulphocamphoric anhydride, obtained by heating the acid with acetic anhydride, crystallises from ethylic acetate in long, colourless needles, melts at $220-222^\circ$, and is nearly insoluble in benzene and chloroform.

$SO_2BrC_8H_{13} \cdot \begin{smallmatrix} CO \\ \diagup \diagdown \\ O \end{smallmatrix}$, the sulphonic bromide of camphoric anhydride, is formed when sulphocamphoric acid is triturated with phosphorus pentabromide. It crystallises from ethylic acetate in minute pyramidal crystals, melting at $169-171^\circ$, and is not appreciably soluble in chloroform or benzene, but dissolves to a slight extent in hot carbon tetrachloride, carbon bisulphide, and xylene. When heated at its melting-point, the sulphonic bromide decomposes into sulphur dioxide and a compound which was proved to be identical with π -bromocamphoric anhydride; this fact shows that sulphocamphoric acid is derived from d -camphoric acid by the substitution of the sulphonic group for one atom of hydrogen.

$SO_2Cl \cdot C_8H_{13} \cdot \begin{smallmatrix} CO \\ \diagup \diagdown \\ O \end{smallmatrix}$, the sulphonic chloride of camphoric anhydride, prepared by treating sulphocamphoric acid with phosphorus pentachloride, crystallises from ethylic acetate in octahedra, needles, or prisms, according to the conditions, and melts and decomposes at 184° ; it resembles the corresponding sulphonic bromide in ordinary properties, and when heated at its melting point it is converted into π -chlorocamphoric anhydride with evolution of sulphur dioxide.

π -Chlorocamphoric acid, $C_{10}H_{13}Cl(COOH)_2$, is obtained by dissolving the crude anhydride in concentrated nitric acid, and then evaporating the solution; it forms beautiful, transparent, apparently orthorhombic crystals, and has no definite melting point, liquefying gradually from about $195-213^\circ$ according to the conditions. This compound is doubtless a derivative of d -camphoric acid, and is therefore an optical isomeride of the π -chlorocamphoric acid which is produced by the oxidation of optically inactive π -chlorocamphor.

π -Chlorocamphoric anhydride separates from a mixture of chloroform and ether in large, transparent prisms, melts at $196-197^\circ$, and resembles π -bromocamphoric anhydride in its general behaviour.

*145. "A Compound of Camphoric Acid and Acetone." By WILLIAM JACKSON POPE.

Detrocamphoric acid crystallises from acetone in large, transparent tablets which belong to the orthorhombic system, and show the forms $\{100\}$, $\{010\}$, $\{110\}$, $\{120\}$, and $\{011\}$; $0.8586 : 1 : 1.2386 = a : b : c$. Although the substance is optically active in solution, no indication of hemihedral structure could be observed. The crystals have the composition $C_{10}H_{16}O_4, \frac{1}{2}Me_2CO$, and in warm weather effloresce slowly, losing their acetone of crystallisation.

These crystals seem to bear no morphotropic relationship to the ordinary monoclinic crystals of camphoric acid, but are closely related to the orthorhombic crystals of camphoric anhydride. If the forms observed on the latter be described as $\{010\}$, $\{001\}$, $\{011\}$, $\{012\}$, and $\{101\}$, the axial ratios become—

$$a : b : c = 1.0027 : 1 : 1.7216;$$

similarly the indices of the forms observed on the compounds of camphoric acid and acetone may be described as $\{010\}$, $\{001\}$, $\{011\}$, $\{012\}$, and 110 , whilst the axial ratios simultaneously change to—

$$a : b : c = 1.2386 : 1 : 1.7172.$$

It thus becomes evident that of the five forms present on each set of crystals, four lying in one zone, namely, {010}, {001}, {011}, and {012}, have the same indices on both; the further remarkable result is obtained that any angle in this zone on crystals of the one substance is practically equal to the corresponding angle in the same zone on the other set of crystals.

*146. "Mercury Hyponitrites." By P. C. RAY, D.Sc.

By the dissociation of mercurous nitrite a neutral solution is obtained containing both mercurous and mercuric nitrites. When this solution is mixed with a dilute solution of sodium hyponitrite, both mercurous and mercuric hyponitrites are apparently formed.

Mercurous nitrate, when similarly treated, does not yield a hyponitrite.

*147. "The Nitrites of Mercury and the Conditions under which they are Formed." By P. C. RAY, D.Sc.

The author finds (1) that mercurous nitrite is always formed by the action of dilute nitric acid (10 to 23 per cent) on mercury at a temperature of about 32°. (2) That the mercurous nitrite thus formed slowly dissolves in the mother liquor, resulting in the production of mercurous nitrate of two kinds:—(a) Monohydrated mercurous nitrate, $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$; and (b) the basic nitrate, named "Marignac's salt." (3) That when a neutral dilute solution of mercurous and mercuric nitrites (the products of dissociation) is allowed to evaporate spontaneously, monohydrated mercurous nitrite, $\text{Hg}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, and two basic mercurous-mercuric nitrites and a basic mercuric nitrite are successively formed. (4) That of these salts only two may be said to contain real "water of crystallisation," namely, those termed monohydrated mercurous nitrite and nitrate respectively, in that they are efflorescent, losing water rapidly in a dry atmosphere. The others apparently contain "water of constitution."

*148. "The Interaction of Mercurous Nitrite and the Alkyl Iodides." By P. C. RAY, D.Sc.

By the interaction of ethyl iodide and mercurous nitrite the author has apparently obtained ethyl nitrite and nitro-ethane.

*149. "Crystallography of the Monohydrated Mercurous Nitrite." By T. H. HOLLAND, F.G.S.

The crystals belong to the triclinic system, and exhibit strong double refraction. Macropinacoidal sections show an extinction angle of 33° to the vertical crystallographic axis.

*150. "On the Identity of Dextrose from Different Sources; With Special Reference to the Cupric Oxide Reducing Power." By C. O'SULLIVAN, F.R.S., and A. L. STERN, D.Sc.

Dextrose was prepared from sugar (cane and beet), starch, and lactose, and the optical activity, the cupric oxide reducing power, and the specific gravity of the aqueous solutions of each specimen determined. These factors were found to be the same for each of the different specimens of dextrose, and consequently from this evidence it is concluded that the dextroses from various sources are identical.

The figures obtained for the cupric oxide reducing power are practically the same as Allihn's, which are in common use in Germany, although the former were obtained by proceeding according to the directions previously given by O'Sullivan, which, however, do not differ materially from Allihn's. A modified form of filtering tube is described, which was found to possess several advantages.

*151. "Note on Mr. W. J. Humphreys' Paper on the Solution and Diffusion of certain Metals in Mercury." By Prof. ROBERTS-AUSTEN, C.B., F.R.S.

In the April number of the *Transactions* (lxix., 243) there is an interesting communication on the above subject by Mr. Humphreys, who is the first to publish results in continuation of Guthrie's experiments (1883) on

diffusion in mercury, and his work is, therefore, very welcome. As, however, I have, at intervals since 1882, conducted experiments on the diffusion of molten metals (Bakerian Lecture, *Phil. Trans.*, 1896, clxxxvii.), I would briefly refer to certain portions of Mr. Humphreys' work that are difficult to interpret by calculation, and I may offer a few suggestions in the hope that they will be useful in future work.

Mr. Humphreys has not attempted to calculate absolute diffusivities from the results of his well-devised experiments. It is, in fact, very difficult to do so, on account of his having used a solid metal instead of a dilute amalgam, from which diffusion into mercury took place. Guthrie did the same, and this precludes the possibility of using the results of either experimenter for calculating absolute diffusivities by the direct application of Stefan's tables (Stefan, *Wien. Akad. Ber.*, 1879; lxxix., 161; see also Roberts-Austen, *loc. cit.*).

Approximate results by calculation appear to show, however, that there is a general concordance between the results of Guthrie and of Humphreys; but more satisfactory results would be afforded if Mr. Humphreys arranged his experiments with a view to their final calculations by means of Stefan's tables.

It is hardly necessary to say that the use of a solid metal diffusing into a fluid one—solid silver into mercury for instance—would introduce the complications arising from the fact that amalgamation or solution of the solid metal must necessarily precede diffusion, and it is very difficult to fix the degree of concentration of the dissolved metal in the layer of amalgam so formed, from which diffusion actually takes place.

Mr. Humphreys states that the rate of diffusion of silver and copper into mercury is 600 times as rapid as that of zinc into mercury, and he expressed a doubt whether this might not be due to superior density of silver amalgam as compared with mercury. Some forty-six years ago, Joule ("Collected Papers," i., 460), working on amalgams of silver and of copper, gave evidence which points to the conclusion that dilute amalgams of these metals would prove to be denser than mercury itself. Mr. Humphreys used single tubes filled with mercury, and silver and copper were respectively placed at the top of fluid columns. The diffusion of silver must be studied by the use of dilute amalgams diffusing upwards, and if, for the purpose of demonstration, Mr. Humphreys will employ U-tubes, as Mr. Stansfield has recently in my laboratory, he will find the amalgamated silver falls rapidly down one limb by density, and slowly rises by diffusion through the mercury in the opposite limb, the diffusivity of silver being, in fact, of the same order as that of zinc which Mr. Humphreys considered to diffuse so slowly.

*152. "Solution and Diffusion of certain Metals and Alloys in Mercury. Part II." By W. J. HUMPHREYS.

The author has extended this investigation (*Proc.*, 1896, xii., 9) to aluminium, antimony, cadmium, magnesium, thallium, and a few alloys. Aluminium and antimony diffuse in mere traces. The cadmium amalgam heavier than mercury was not formed. The author considers that solution and diffusion in mercury may serve to distinguish between mixtures and compounds in the case of alloys. Metals that belong to the same group in Mendeleeff's table increase in their power of solution and diffusion with their atomic weight.

*153. "Note on the Heat of Formation of the Silver Amalgam, Ag_2Hg_8 ." By FANNIE T. LITTLETON.

In a previous communication (*Trans.*, 1895, lxvii., 239) an account was given of a silver amalgam exhibiting remarkable behaviour on being moderately heated, swelling up as if from the evolution of gas, and becoming hard, brittle, and crystalline in structure. It was noted that this behaviour was most marked when the silver and mercury were present in the ratio of 1 atom of the former to 4 of the latter, and that, when these metals were

brought together, the silver in the state of a fine crystalline powder (as reduced from the pulverulent chloride by zinc and a little hydrochloric acid), and the mercury simply poured over it, there was very considerable rise of temperature, amounting to 38° or 40° , so that the amalgam could not be borne on the palm of the hand without pain.

No actual measurement of the heat evolved in the formation of the amalgam was made. Such measurements have recently been made in a simple form of calorimeter, with the following result:—

If the formula assumed for the amalgam be Ag_2Hg , and the molecular weight be taken as 1813.8 ($H=1$), the heat evolved in the formation of 1 molecule is equal to about 3432 units, the molecular weight being counted in grms., and the unit of heat as the heat required to raise the temperature of 1 grm. of water (at about 22°) by 1° . These determinations gave the values 3395, 3418, and 3484. It is to be observed that the amalgam, just after its production, is a soft, pasty, semi-fluid mass. Calculating from Person's figures, for the latent heat of fluidity of the metals concerned, 1813.8 grms. of the amalgam consists of 215.4 grms. of silver, the fusion of which would absorb 4537 heat units and 1598.4 grms. of mercury, the solidification of which would evolve 4507 heat units.

Two nearly-agreeing determinations of the specific heat of the amalgam, in its freshly-formed condition, gave an average value of 0.029 referred to an equal weight of water as unity. This is notably below 0.0359, the result of calculation from the specific heats of the respective metals, assuming these to remain unchanged in the amalgam.

154. "Preliminary Note on the Action of Alkyl Iodides on Silver Malate." By THOMAS PURDIE, F.R.S., and G. DRUCE LANDER, B.Sc.

In a recent communication to the Society (Purdie and Williamson, *Trans.*, 1896, lxix., 818), on the optical activity of ethereal malates and lactates prepared by different methods, it was shown that, while the action of methylic, ethylic, *n*-propylic, and *n*-butylic iodides on silver malate proceeded apparently in the normal manner, the action of isopropylic iodide was anomalous. The ethereal salt obtained from the latter reaction was small in quantity; the percentages of carbon and hydrogen found on analysis were considerably higher than the numbers calculated for isopropylic malate, and the liquid showed a much higher activity than this substance should possess. The authors have repeated the experiment on a larger scale, and find that the high activity of the product is due to the presence in it of about 20 per cent of isopropylic isopropoxysuccinate. It appears that the isopropyl group of the iodide replaces not only the silver of the malate, but also, to a considerable extent, the hydrogen of its alcoholic hydroxyl.

The isopropylic isopropoxysuccinate was obtained by the partial hydrolysis of the product of the reaction, the malate being more easily hydrolysed than the other compound. The rotation of the mixture produced by the reaction was $\alpha = -32.96^{\circ}$ ($l=1$), that of the isopropoxysuccinate was -57.08° . The results of the analysis of the ethereal salt, and also of the barium, calcium, and potassium salts obtained from it, were in agreement with the calculated numbers. The specific rotations in aqueous solutions of varying concentration were determined for the acid, also for the barium, calcium, acid potassium and normal potassium salts, and were found in general to approximate to the corresponding numbers for active normal propoxysuccinic acid prepared by resolution of the inactive compound (*Trans.*, 1895, lxvii., 949).

In the paper on ethereal malates and lactates (*loc. cit.*) it was pointed out that the ethereal salts made from the silver salt possessed in every case a notably higher activity than those made by the hydrochloric and sulphuric acid methods. The obvious conclusion that the

difference was due to the presence of racemoid substance in the latter compounds was negated by experiments which failed to detect in them such a quantity of racemoid compound as would account for their lower activity. The cause of the anomaly was left unexplained. After the authors had discovered, however, that isopropoxysuccinic acid was produced in considerable quantity by the reaction of isopropylic iodide on silver malate, it seemed probable that the higher activity of the other malates, made by the same method, might also be due to their being contaminated with small quantities of the corresponding alkoxysuccinates. In the case of ethylic malate an admixture of about 4 per cent of ethylic ethoxysuccinate would suffice to account for the higher observed activity; its presence could not be detected by analysis, nor in the course of ordinary fractional distillation, the differences in the boiling-points of the substances being inconsiderable.

To test the correctness of the suggested explanation, the authors prepared ethylic malate from the silver salt on a large scale. The crude product boiled at $130-135^{\circ}$ at about 15 m.m., and showed the activity $\alpha = -13.93^{\circ}$ ($l=1$). On re-distillation, the activity of the first fraction collected showed a rise of about 1° , and after often-repeated fractional distillation, two fractions were finally obtained, differing in boiling-point by only about 3° , the lower boiling fraction, however, having the activity $\alpha = -17.05^{\circ}$ ($l=1$) and the higher boiling $\alpha = -12.26^{\circ}$. By partial hydrolysis of the former fraction the activity of the unhydrolysed oil was raised to -20° . The rotation of ethylic malate made by the mineral acid methods was previously found to be $\alpha = 11.7^{\circ}$. The ethylic malate made by the silver salt method is, therefore, evidently contaminated with a small quantity of a much more active compound, and although efforts to isolate the substance in the pure state have so far been unsuccessful, it is very probable, judging from the case of isopropylic iodide, that the compound in question is ethylic ethoxysuccinate.

Experiments show that the ethereal salts of malic acid, and, no doubt, of other hydroxy-acids, cannot be obtained in the pure state from the silver salt; by the action of isopropylic iodide, isopropylic isopropoxysuccinate is produced in quantity, and the higher activities found for other malates prepared by this method, which are quoted in the paper referred to, are due probably to the presence of small quantities of the ethereal salts of the highly active alkoxo-acids. The high activity of the ethereal lactates made from the silver salt, which the authors are at present examining, will probably find a similar explanation.

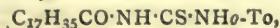
The authors are not aware that the production of alkoxo-acids by the action of alkyl iodides on silver salts of hydroxy-acids has ever been observed. The reaction is remarkable, and the authors are investigating it further.

155. "On certain Thiocarbimides derived from Complex Fatty Acids." By AUGUSTUS E. DIXON, M.D.

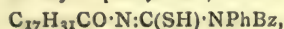
In this paper an account is given of the preparation of thiocarbimides derived from palmitic and stearic acids; the compounds in question, if brought into contact with organic bases, afford the corresponding substituted thiocarbimides, or thioureas; from these, in turn, by suitable treatment with silver compounds, their oxygen analogues may be obtained.

Palmitylthiocarbimide, $\text{C}_{15}\text{H}_{31}\text{CO}\cdot\text{NCS}$, is an easily fusible, soft solid, of faintly pungent odour; it distils, with considerable decomposition, between 200° and 205° , and is attacked by water, yielding palmitic and thiocyanic acids. *ab*-Palmitylphenylthiocarbimide, $\text{C}_{15}\text{H}_{31}\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, crystallises from alcohol in slender, waxy-looking needles, insoluble in water, soluble in the ordinary organic solvents, and melting at $62-63^{\circ}$ (uncorr.). The corresponding urea forms microscopic needles; *m. p.* $90-91^{\circ}$. *ab*-Palmitylorthotolylthiocarba-

amide, $C_{15}H_{31}CO \cdot NH \cdot CS \cdot NH_2 \cdot To$, felted white needles, melting between 65.5 and 66.5° . The urea occurs in woolly masses of flexible needles; m. p. 98° . ab-Palmityl-paratolylthiocarbamide, and palmitylparatolylurea, fine needles, melting at $75-76^\circ$, and $89-90^\circ$ respectively. $C_{15}H_{31}CO \cdot N : C(SH) \cdot NMePh$, n-palmityl-v-methylphenylthiourea, white needles; m. p. $59-60^\circ$. n-Palmityl-v-phenylbenzylthiourea, $C_{15}H_{31}CO \cdot N : C(SH) \cdot NPhBz$, was obtained in nearly quantitative amount; it melts at $62-63^\circ$, and by desulphurisation affords the urea, $C_{15}H_{31}CO \cdot NH \cdot CO \cdot NPhBz$, pearly needles of m. p. $68-69^\circ$. ab-Stearylorthotolylthiocarbamide,—



is deposited from absolute alcohol in very fine white needles, melting at $67-68^\circ$; by treatment with silver nitrate it affords stearylorthotolylurea, m. p. $94-95^\circ$. $C_{17}H_{35}CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5 \cdot Me_2$, ab-stearylmetaxylylthiocarbamide, lustrous needles, melting at $71-72^\circ$; the corresponding urea melts at $92-93^\circ$. ab-Stearylalphanaphthylthiocarbamide, melts at $80-81^\circ$; the urea at $114-115^\circ$. n-Stearyl-v-phenylbenzylthiourea,—



melts at $66-66.5^\circ$. and by desulphurisation affords the urea, $C_{17}H_{35}CO \cdot NH \cdot CO \cdot NPhBz$; the latter forms white needles, becoming electrical on friction, and melting between 74 and 75° .

It is stated by Miquel (*Ann. Chim. Phys.*, [5], xi., 316) that benzoylthiocarbimide, $PhCO \cdot NCS$, even if heated at 200° with diethylamine, remains unaltered; the author finds, however, that solutions of these two substances, in benzene and alcohol respectively, interact spontaneously, with marked evolution of heat, and production of n-benzoyl-v-diethylthiourea, $PhCO \cdot N : C(SH) \cdot NEt_2$. The latter forms long, brilliant prisms, sparingly soluble in boiling water; m. p. $100-101^\circ$ (corr.).

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

First Ordinary Meeting, November 30th, 1896.

Prof. A. CRUM BROWN, President, in the Chair.

THE PRESIDENT opened with his Inaugural Address, taking as his subject "The Life and Work of Kekulé."

He first referred to the fact that since the last address he had given to the Society there had passed away one of the most distinguished chemists of his time.

After a short sketch of Kekulé's life, Professor Crum Brown referred to the most important of his discoveries and speculations:—The Quadrivalence of Carbon, the Constitution and Relation of Maleic, Fumaric, and Succinic Acids, and of Citraconic, Itaconic, Mesaconic, and Pyrotartaric Acids; the Constitution of Benzene and of Aromatic Compounds generally. He stated his belief that even now, after the enormous extension of aromatic chemistry due to Kekulé's ideas, Kekulé's original formula for benzene remains, on the whole, the most satisfactory.

Among the later works of Kekulé, his investigation into the so-called carboxyltartronic acid was discussed in its bearings on the constitution of benzene.

In conclusion, the President indicated to how great an extent our present ideas and our present knowledge of the facts of organic chemistry are directly due to Kekulé or to his influence, and recommended a study of his individual papers. These are not very numerous, but every one is of a classical character.

Distribution of Lipase in the Organism.—M. Hanriot.—It results that the lipasic ferment is absent in most of the organs except in the pancreas and liver.—*Comptes Rendus*, cxxiii., No. 20.

NOTICES OF BOOKS.

The Gases of the Atmosphere: their History and their Discovery. By WILLIAM RAMSAY, F.R.S., Professor of Chemistry in University College, London. With Portraits. London: Macmillan and Co. (Ltd.). New York: The Macmillan Co. Pp. 240. 1896.

In his Preface the author reminds us that the discovery of argon, in 1894, re-opens a chapter in chemistry which had been considered as closed,—that is, the composition of the atmosphere and the number and the attributes of its ingredients. The accounts of the gas as submitted to the Royal Society, by Lord Rayleigh and Prof. Ramsay, and verified by other chemists and physicists, were written in a style adapted to experts only, and the paraphrases of these first announcements which figured in popular organs were—as usual in such cases—lacking in precision. Hence the author finds it desirable to submit to the public a correct account of this discovery and of the steps by which it has been reached. In so doing he has expounded the results of earlier experiment and speculation concerning the composition of the atmosphere. In this study we are introduced to some eminent men of Science,—Boyle, Mayow, and Hales,—now most undeservedly forgotten. These investigators, we find, were all Oxford men. In those days Oxford had not lost sight of the beacon light raised by the elder Bacon, which we may hope she is beginning to again recognise. The early death of Mayow—lost to Science in his thirty-fourth year—is justly deplored. It appears not unlikely that, had he reached an average age, he would have anticipated the illustrious Lavoisier, and the world might thus have been spared the delusions of the Phlogistian School. The rise and persistence of this School was particularly unfortunate for English Science. Hales and Priestley were both experimentalists, but they derived little benefit either from their own experiments or from those of Mayow.

The next forward step in pneumatic chemistry was Black's discovery of carbon dioxide—the first ingredient of the air which was definitely recognised, and was not again lost sight of as was Mayow's "fire-air." Daniel Rutherford, a pupil of Black, is here duly credited with the discovery of nitrogen, or, as it was called, "phlogisticated air." Cavendish unfortunately did not appeal to the balance to check his results.

With the avatar of Lavoisier's new system of chemistry—"la chimie Française" as it was called by some—the study of the atmosphere was laid aside as complete. But in 1882 Lord Rayleigh, in his presidential address to the Physical Section of the British Association, referred to an investigation on the relative densities of hydrogen and oxygen. His object was to ascertain whether the atomic weight of these gases, as determined from their densities and combining volumes, were exactly as 1:16. After prolonged experimentation he came to the conclusion that the atomic weight of oxygen must be 15.882, hydrogen being 1. The percentage of oxygen must be 20.941, and that of nitrogen 79.059, to give a mixture a litre of which weighs 1.29327 grms. For these experiments the nitrogen was prepared by several methods. It was then found that nitrogen obtained by the decomposition of ammonia was somewhat lighter than atmospheric nitrogen, the deficiency being about 1 part in 200. Further experiments showed that in every case the nitrogen, from all sources except the atmospheric, weighed rather less than atmospheric nitrogen. Lord Rayleigh now found that the atmospheric nitrogen contained a residuum of a gas which, unlike pure nitrogen, would not disappear on "sparking" with oxygen in presence of caustic soda.

By the meeting of the British Association at Oxford (August, 1895) the evidence for the presence of a new constituent gas in the atmosphere was such as to warrant its publication. It was received with interest, not un-

mixed with scepticism. One of the audience put the curious question, whether the name of this new substance had been discovered? It was found that the new substance (to which the name of argon had been ascribed, from its chemical inertness) is present only in the atmosphere, in the gases extracted from certain mineral waters, in one meteorite, and in a few more minerals. It does not appear to be present in any appreciable proportion in any animal or vegetable matter; nor does it appear to have any action upon living organisms.

Among the mineral waters richest in argon are those of Bath and Buxton, and Allhusen's Well at Middlesborough.

Helium, which has properties rather similar to those of argon, is not found in the atmosphere.

Prof. Ramsay's work is of exceeding interest as showing the niceties demanded in such investigations. Hence it will prove a most instructive study for chemical students of all ages.

thus revealed in their properties and reactions from those of elementary carbon in its amorphous forms.

These results are fully recorded in a series of publications, viz., *Journ. Chem. Soc.*, xli, 103; xliii., 21; *Phil. Mag.*, v., 13, 325; 14, 346; *Brit. Assoc. Report*, 1881,—of the existence of which we have reason to know the Committee was aware.

The report, upon the basis of its contribution of new matter, cannot make any claim to have advanced our knowledge of the coals beyond the point to which it was carried fifteen years ago.

Without insisting on the personal aspect of the matter, the form of the report amounts to a deliberate setting aside of scientific records, and although we have a particular objection to "priority grievances," and should never raise a question where an obvious oversight is involved, the present case leaves us no alternative but to protest.—We are, &c.,

CROSS and BEVAN.

4, New Court, Lincoln's Inn, W.C.,
December 7, 1896.

CORRESPONDENCE.

THE PROXIMATE CONSTITUENTS OF COAL

To the Editor of the Chemical News.

SIR,—The report of the B.A. Committee of investigation of the above subject, published in recent issues of the *CHEMICAL NEWS* (vol. lxxiv., pp. 261, 271), puts us in the unpleasant position of having to deal with a question of priority.

The only "new" matter in the report is contained in results of chlorination methods applied to the coals. The "composition and physical properties of the chlorinated compounds obtained," the report mentions incidentally, "recall those described by Messrs. Cross and Bevan in their investigations of jute."

This re-discovery of our results of fifteen years ago we note as a confirmation of ancient work: we make no protest on this ground. What we do object to is the much larger *suppressio veri*. The facts are these:—

In 1880–82 we extended the methods of enquiry which we had found useful in resolving the problem of the constitution of the ligno-celluloses specifically to the coals, regarded as extreme terms of the series of natural condensation products of the celluloses. We isolated from the coals a series of chlorinated compounds having identical features with those described in the report in question. We obtained from the celluloses, by the action of H_2SO_4 at 70° , products of condensation separating as gelatinous hydrates and passing by spontaneous dehydration into black lustrous solids, having all the external characteristics of the coals, from which chlorinated derivatives were obtained, one of which had the formula $\text{C}_{21}\text{H}_{16}\text{Cl}_4\text{O}_{10}$. We showed the connection of these compounds with the "humic" series of condensation products of the carbohydrate group, obtained by both natural and artificial processes, which also yield products of chlorination similar in composition and identical in characteristics (Sestini). We studied the action of nitric acid on the coals, and showed that substitution derivatives were obtained, and also we called attention to a remarkable paper of Hatchett's, published in the *Phil. Trans.* in 1805, dealing with the action of nitric acid on a wide range of "organic" compounds of this class. We also studied the action of sulphuric acid on these condensation products, and showed that its deoxidation to sulphurous acid was accounted for by a sulphonation of CH residues (as a first stage in the deoxidation), followed by oxidation of the C atoms themselves. We also proposed to designate this group of "carbonaceous" compounds by the term "pseudo-carbon," to emphasise the difference

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 20, November 16, 1896.

Researches on Phosphoric Acid. Determination of Pyrophosphoric Acid.—M. Berthelot and G. André.

Transformation of Pyrophosphoric Acid.—M. Berthelot and G. André.—These two connected papers will be inserted in full.

On the Earths of the Yttria Group contained in the Monasite Sands.—P. Schützenberger and Boudouard.—This paper also will be inserted *in extenso*.

Densities of Nitrogen, Oxygen, and Argon, and the Composition of Atmospheric Air.—A. Leduc.—The discovery of argon has modified a number of the results formerly published by the author: atomic weights, molecular volumes, and especially the density of nitrogen. He had besides been led to resume the study of some gases, and particularly that of oxygen, the density of which appears slightly too low in comparison with chemical nitrogen. His new experiments show the density of nitrogen in comparison with atmospheric air as 0.96717. For the density of oxygen he admits the figure 1.10523, being convinced of the insufficiency of platinum sponge. Argon.—For the proportion of argon in atmospheric air he finds 0.0119, and for its density 1.376. The mean composition of atmospheric air is shown in the following table:—

	Nitrogen.	Oxygen.	Argon.
By weight	75.5	23.2	1.3
By volume	78.06	21	0.94

Cock for Receivers destined for Compressed or Liquefied Gases.—E. Ducretet and L. Lejeune.—The structure of this appliance cannot be shown without the accompanying figure.

Neutrality of Salts and Coloured Indicators.—H. Lescœur.—(See p. 285).

Analysis of Air by Agaricus atramentarius.—Dr. T. L. Phipson.

Some Properties of Pure Glucina.—P. Lebeau.—Pure glucina is fusible and volatile at the temperature of the electric furnace. It does not vary appreciably in density, and retains the property of being attackable by concentrated acids. Boron, silicon, and carbon are the

only non-metals capable of reducing glucina and yielding crystalline compounds. The reductive metals—sodium, potassium, magnesium, and aluminium, have no action.

Action of Sulphuric Acid and Iodine upon Iodic Acid.—Paul Chretien.—By this reaction the author obtains crystals containing when dry 99.6 per cent of iodic anhydride. He finds in 100 parts—

Iodine liberated by water	25.98
Iodine remaining as iodic acid.. .. .	38.07
Oxygen.. .. .	12.17
Sulphuric anhydride	20.46
Water	2.3

99.98

Ratio of iodine to oxygen 5.291.

Molybdenum Iodide.—M. Guichard.—Molybdenum iodide, MoI_2 , may be prepared in the amorphous state by the action of hydriodic acid upon molybdenum chloride.

Separation of Tungsten from Titanium.—Ed. Defacqz.—The sample, whether a mixture of the two acids, calcined, or not, or an alloy, is treated in a platinum crucible with 7 to 8 times its weight of a mixture of 8 parts potassium nitrate and 8 parts potassium carbonate. It is heated to dull redness for twenty to thirty minutes, when there is obtained a white mass, which, when cold, is taken up in water. The product is evaporated to dryness in the water-bath. It is washed at first by decantation, and the insoluble part is further washed upon the filter with water containing ammonium nitrate. In the liquid to which the washings have been added the tungsten is determined as mercurous tungstate with the usual precautions. The residue on the filter is dried and ignited, and treated with potassium bisulphate, in order to determine the titanium in the general manner.

Spectrum of the Chlorophylls.—A. Etard.—This paper will be inserted in full.

Fixation of Atmospheric Nitrogen by the Association of Algae and Bacteria.—Raoul Bouilliac.—The author's experiments show that *Schizothrix lardacea* and *Ulothrix flaccida* cannot grow in nutrient solutions void of nitrogen, even in presence of the bacteria of the soil. It is quite otherwise with *Nostoe punctiforme*. The association of this alga with the bacteria permits the simultaneous development of the two species and the fixation of nitrogen ensues most distinctly. Both the *nostoe* and the bacteria in question can flourish in a solution containing 1/10,000 of arsenic.

Organic Matter in the Mineral Water of Tulba-Haut (Haute Garonne).—F. Garrigou.—The author records the presence of an organic alkaloid as more distinct than in any other mineral water.

Zeitschrift fur Analytische Chemie.
Vol. xxxv., Parts 4 and 5.

Detection of Sugar.—Neitzel (*Deutsch. Zucker Industrie und Chemiker Zeitung*).—The author substitutes camphor for α -naphthol.

Determination of Nitrogen in Organic Substances.—C. E. Zay and Haselhoff (*Chemiker Zeitung*).—Modifications of the Kjeldahl process.

Relations of Contraction on mixing Acetone with Water.—K. P. McElroy.—The greatest contraction is 4 per cent.—*Journ. Am. Chem. Soc.*

Volumetric Determination of Hydroxylamine by means of Solution of Iodine.—Tamemasa Haga.—From the *Journal of the Chemical Society*.

Determination of Parasulphanilic Acid.—K. Brenzinger (*Zeit. Angewandte Chemie*).—Parasulphanilic acid, on treatment with nascent bromine or bromine-water, is converted into tribromaniline with abscission of sulphuric acid. Orthosulphanilic acid behaves in a similar manner.

The author proceeds as follows:—A quantity corresponding to about 1.73 grms. sulphanilic acid is dissolved in about 100 c.c. of water, slightly acidified, and saturated bromine water is added until a distinct reaction is obtained on potassium iodide starch-paper, like that assumed at the conclusion of a diazotation. It is allowed to stand for about thirty minutes. It is then rendered distinctly alkaline with ammonia or sodium carbonate, heated almost to ebullition, and filtered. In the filtrate the sulphuric acid formed is determined in the usual manner. The precipitation, filtration, and washing of the barium sulphate must be effected in as great a heat as possible, especially if metasulphanilic acid is the predominating ingredient.

Determination of Value of Naphtholic and Naphthylaminic Sulpho-Acids.—W. Vaubel (*Chem. Zeit.*).—The author has extended his process to a number of new components.

Colorimetric Determination of Carbohydrates.—Neitzel.—This method has been patented by the author (!)

Determination of Cane-sugar in presence of Milk-sugar.—W. D. Bigelow and K. P. McElroy.—From the *Journ. Am. Chem. Soc.*

Determination of pre-existing Sugar in Green Malt.—J. Jais.—A combination of the two methods already known.

The Chemical Composition of Fruit-Wines and their Distinction from Grape-Wines.—Kuhlisch (*Chemiker Zeitung*).—The alcohol per cent in ciders is low, ranging from 4.29–5.86 per cent, but the extractive and mineral matters are higher than in grape-wines. The tannin is very slightly higher than in white grape-wines, but the nitrogen is considerably lower. The only certain distinction between fruit and grape wines is that the former contain no tartaric acid nor its salts. Certain American and English ciders and perries contain much unfermented sugar (*Embrey, Analyst*). White and red currant wines prepared by the addition of sugar to the fruit juice before fermentation may contain 13 grms. alcohol in 100 c.c., and only 0.007 phosphoric acid.

MISCELLANEOUS.

Society of Public Analysts.—The following nominations have been made for Officers and Council for the year 1897.

President—Bernard Dyer, D.Sc.

Vice-Presidents (who have filled the office of President)

—M. A. Adams, F.R.C.S.; A. H. Allen; Sir Charles A. Cameron, M.D., F.R.C.S.; A. Dupré, Ph.D., F.R.S.; Otto Hehner; Alfred Hill, M.D., F.R.S.E.; J. Muter, M.A., Ph.D., F.R.S.E.; Thos. Stevenson, M.D., F.R.C.P. (Who have not filled the office of President)—A. P. Aitken, D.Sc., F.R.S.E.; W. W. Fisher, M.A.; John Pattinson, Treasurer—E. W. Voelcker.

Hon. Secretaries—E. J. Bevan; Charles E. Cassal.

Other Members of Council—R. Bodmer; A. Wynter Blyth, M.R.C.S.; A. C. Chapman; S. Rideal, D.Sc.; J. E. Stead; J. A. Voelcker, M.A., B.Sc., Ph.D.

The names of those Members of Council who do not retire this year are—Leonard Archbutt, Bertram Blount, E. Russell Budden, W. J. Dibdin, Sidney Harvey, and Alfred Smetham.

Royal Institution.—His Royal Highness the Prince of Wales has consented to open on Tuesday afternoon, December 22nd, 1896, the Davy-Faraday Research Laboratory of the Royal Institution, founded by Dr. Ludwig Mond, F.R.S., as a memorial of Davy and Faraday. The ceremony will take place in the theatre of

the Royal Institution, where, by desire of His Royal Highness, Professor Dewar will after the opening ceremony show experiments illustrative of the use of "Liquid Air in Scientific Research." The following are the lecture arrangements before Easter:—Professor Silvanus P. Thompson, six lectures (adapted to a Juvenile Auditor) on "Light, Visible and Invisible"; Professor Augustus D. Waller, twelve lectures on "Animal Electricity"; Professor Henry A. Miers, three lectures on "Some Secrets of Crystals"; Dr. J. W. Gregory, three lectures on "The Problems of Arctic Geology"; Professor Percy Gardner, three lectures on "Greek History and Extant Monuments"; Professor W. Boyd Dawkins, three lectures on "The Relation of Geology to History"; Mr. Carl Armbruster, three lectures on "Neglected Italian and French Composers"; Mr. Walter Frewen Lord, three lectures on the "Growth of the Mediterranean Route to the East"; and the Right Hon. Lord Rayleigh, six lectures on "Electricity and Electrical Vibrations." The Friday Evening Meetings will begin on January 22nd, when a discourse will be given by Professor Dewar; succeeding discourses will probably be given by The Right Rev. The Lord Bishop of London, Professor Jagadis Chunder Bose, Professor John Milne, Dr. G. Johnstone Stoney, Lieut.-Col. C. R. Conder, R.E., Mr. Shelford Bidwell, Professor Arthur Smithells, Sir Edward Maunde Thompson, Sir William Turner, Mr. Charles T. Heycock, the Right Hon. Lord Rayleigh, and other gentlemen.

MEETINGS FOR THE WEEK.

WEDNESDAY, 16th.—Society of Arts, 8. "The Chamber Music of Purcell, Handel, and Bach," by Arnold Dolmetsch.

THURSDAY, 17th.—Chemical, 8. "Experimental Methods employed in the Examination of the Products of Starch Hydrolysis," "Specific Rotation of Maltose and of Soluble Starch," "Relation of the Specific Rotatory and Cupric Reducing Powers of Starch Hydrolysis by Diastase," by Horace T. Brown, F.R.S., G. H. Morris, Ph.D., and W. H. Millar.

A Gentleman requires Berth as Analytical or Manufacturing Chemist. Has no objection to position in Colonies. Salary moderate.—Apply, E. H., CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

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THE CHEMICAL NEWS.

Vol. LXXIV., No. 1934.

NOTE ON A CASE OF POISONING BY ARECA NUT.

By ERNEST H. COOK, D.Sc., (Lond.), A.R.C.S.,
Clifton Laboratory, Bristol.

THE powdered nut of *Areca Catechu* is largely used in veterinary practice as a tenicide, and is in especial favour with those amateurs who are accustomed to treat their own dogs for an attack of worms. Cases of poisoning following its use are rare, and the following particulars of one which has recently been met with in ordinary analytical practice are therefore communicated.

A teaspoonful of areca nut in fine powder (about 56 grains) was added to half a teacupful of castor oil, and administered to four Dachshund puppies of the same litter aged five months. So far as can be ascertained the substances were thoroughly mixed, and approximately equal amounts given to each. All the dogs were highly bred and in fairly good health previously. In less than five minutes after administration they were seen to be in distress. They had great difficulty in breathing, coughed slightly, and fell down on one side. Locomotion was only possible with difficulty. Seeing their condition the owner endeavoured to administer salt and water as an emetic. This was successful in two cases, but not in the others. The latter gradually got weaker, became unable to rise, and died in ten minutes. No convulsions or convulsive twitchings occurred. Respiration gradually became more and more difficult until death quietly ensued, intelligence being maintained until the end. The bowels were not moved. A third dog died after languishing for five hours, notwithstanding the successful administration of the emetic.

On post-mortem examination the stomach was found to be slightly inflamed, the inflammation being general and not in patches. The trachea and some of the lung passages were filled with a dense white froth. The left ventricle was found gorged with blood, as was also the aorta and left auricle. The right auricle and ventricle were comparatively empty. The other organs were normal. The iris showed no alteration from its normal size.

The contents of the stomach were extracted with weak alcohol and dilute acetic acid, and the usual tests for the more commonly occurring alkaloids applied. (This was done because the owner, who has been in the habit of frequently giving areca nut to his dogs, was of opinion that that substance could not be the cause of death, but that some more powerful poison must be present). None of these were found, but Mayer's reagent gave an alkaloidal precipitate with the extract. The amount of substance available was, however, so small that beyond this no confirmation of the presence of the arecoline—the poisonous alkaloid in areca nut—was possible. The whole circumstances of the case, as well as the absence of the other alkaloids and mineral and other poisons, all of which were unsuccessfully tested for, can leave no doubt that death was caused by the nut.

Assuming that each dog had an equal quantity, the amount was approximately 14 grains. It is, however, quite a common thing for doses of a drachm (60 grains) to be administered without ill effect.

It would thus appear that the action of the substance is uncertain, and that its employment therefore requires great care.

It should be mentioned that the unused portion of the

sample was sent for analysis and thoroughly examined, but no poisonous substance other than that in the areca nut could be discovered.

USE OF THE X RAYS FOR ANATOMICAL RESEARCH: ANGEIOLOGY, DEVELOPMENT, OSSIFICATION, EVOLUTION OF TEETH, &c.

By CH. REMY and G. CONTREMOULINS.

WE have the honour of submitting to the Academy a series of radiographs taken on the dead body, in which we observe anatomical details not hitherto recognised. We wish to speak of the disposition of the arterial system down to its finest sub-divisions.

In the figure, which represents the hand with its forearm and a part of the arm, we may follow in their relations with the osseous system the divisions of the arteries, the collaterals of the fingers up to the vascular tufts of the digital pulp. We may also follow the penetration of the arteries into the bony tissue.

In the parts which we have submitted to radiography the veins are not apparent, but we may obtain their image by the procedure which we have made use of.

Professor Marey has suggested to us the idea of rendering the vascular system opaque to the X rays by injecting them with a liquid holding in suspension impalpable metallic powders; a great variety of such powders are now met with in commerce under the name of bronzes. The medium which we employed is common sealing-wax dissolved in alcohol; the injection is performed in the cold.

We emphasise the importance of the results of this method, which gives the distribution of the vessels with their real situation and relations which are always altered by dissection. In order to seize the different degrees of depth of the vascular planes we have employed stereoscopic proofs, the aspect of which is striking.

In the same figures, thanks to the Collardeau tube and the Gaiffe coil, the outlines are perfectly distinct as well as the details of the structure of the bones.

One of our figures represents the lower half of the body of a human fœtus on which the position of the points of ossification is very well determined.

In another figure, representing the half of the lower jaw of a child of 7 years, we see distinctly the four molars with their layer of enamel, the dentine, the dentary pulp, and the channels of the nerves; whilst at the base of the ascending branch the wisdom-tooth, in its closed cell, awaits the time of its appearance.—*Comptes Rendus*, cxxiii., p. 711.

AN ATTEMPT TO DETERMINE THE ADIABATIC RELATIONS OF ETHYL OXIDE.*

By E. P. PERMAN, D.Sc., W. RAMSAY, Ph.D., F.R.S., and
J. ROSE-INNES, M.A., B.Sc.

THE wave-length of sound in gaseous and in liquid ethyl oxide (sulphuric ether) has been determined by the two first-mentioned of the authors, by means of Kundt's method, between limits of temperature ranging from 100° C. to 200° C., and of pressure ranging from 4000 to 31,000 m.m. of mercury, and of volume ranging from 2.6 c.c. per grm. to 71 c.c. per grm. Making use of the same apparatus throughout, the results obtained are to be regarded as comparative, and, by careful determination of the pitch of the tone transmitted through the gas, it is probable they are approximately absolute.

* Abstract of a Paper read before the Royal Society, Dec. 10, 1896.

The sections of the complete memoir deal with (I.) a description of the apparatus employed, (II.) the method of ascertaining the weights of ether used in each series of experiments, (3) determinations of the frequency of the vibrating rod, (IV.) the calculations of the adiabatic elasticity and tables of the experimental results, and (V.) a mathematical discussion of the results. The last section is due to Mr. Rose-Innes.

As the theoretical results are of interest, a brief outline of them may be given here.

It will be remembered that one of the authors, in conjunction with Dr. Sydney Young, showed that for ether, and for some other liquids, a linear relation subsists between pressure and temperature, volume being kept constant, so that—

$$p = bT - a.$$

It has been found that a similar relation obtains between adiabatic elasticity and temperature, volume, as before, being kept constant: so that, within limits of experimental error, where E stands for adiabatic elasticity,—

$$E = gT - h,$$

g and h being functions of the volume only. Between these two equations, we may eliminate T , and so express E as a linear function of p , volume being kept constant. The coefficient of p in such an equation would be g/b , and this fraction, on being calculated from the data available, proves to be nearly constant. For working purposes it is assumed that g/b may be treated as strictly constant, and it is shown that this assumption does not introduce any serious error within the limits of volume considered. We then find it possible to integrate the resulting differential equation, and the complete primitive enables us to draw a set of adiabatic curves. We believe that this is the first time adiabatic curves have been obtained for any substance except perfect gases.

A mathematical discussion is added as to what extent the equations—

$$E = gT - h$$

and—

$$g/b = \text{constant},$$

can be considered as strictly true, and not merely approximate.

The experimental results for liquid ether form an appendix to the paper.

A METHOD FOR THE SEPARATION OF ALUMINUM FROM IRON.

By F. A. GOOCH and F. S. HAVENS.

Of the well-known methods for the separation of aluminum from iron—by the action, for example, of an alkaline hydroxide in aqueous solution, or by fusion of the mixed oxide in potassium or sodium hydroxide; by reduction of the iron oxide to the metal by heating in hydrogen, with the subsequent solution of the metallic iron in hydrochloric acid; by boiling the nearly neutral solution of the salts of aluminum and iron with sodium thiosulphate either with or without sodium phosphate; by acting with hydrogen sulphide or ammonium sulphide upon solutions of the salts containing also an ammoniacal citrate or tartrate—no single process can be said to be ideal as regards directness, rapidity, and accuracy of working. We have deemed it not superfluous, therefore, to attempt the utilisation of a reaction which should apparently be capable of effecting directly and quickly the separation of aluminum from iron under conditions easily attainable.

It is known (Gladysz, *Ber. d. d. Chem. Gesell.*, xvi., 447) that the hydrous aluminum chloride $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is

very slightly soluble in strong hydrochloric acid, while ferric chloride, on the other hand, is extremely soluble in that medium. It is this difference of relation of which we wished to take advantage.

It appeared at the outset that crude aluminum chloride could be freed from every trace of a ferric salt by dissolving it in the least possible amount of water, saturating the cooled solution with gaseous hydrochloric acid, filtering upon asbestos in a filtering crucible or cone, and washing the crystalline precipitate with the strongest hydrochloric acid. Aluminum chloride prepared in this way gave no trace of colour when dissolved in water and tested with potassium sulphocyanide. The correlative question as to how much aluminum chloride goes into solution under the conditions was settled by taking a portion of the pure aluminum chloride, dissolving it in a very little water, diluting the solution with strong hydrochloric acid, saturating the cooled liquid with the gaseous acid, filtering on asbestos, precipitating by ammonia the aluminum salt in the filtrate, and weighing the ignited oxide.

From 10 c.m.³ of such a filtrate we obtained in two determinations 0.0022 grm. and 0.0024 grm. of the oxide, the mean of which corresponds to 23 parts of the oxide, or 109 parts of the hydrous chloride in 100,000 parts of the strong hydrochloric acid. This degree of solubility, though inconsiderable when the objective point is the preparation of the pure salt of aluminum, is obviously incompatible with the attainment of quantitative accuracy in the retention of the aluminum. We have found, however, that various mixtures of anhydrous ether and the strongest hydrochloric acid can be used satisfactorily as solvents for the iron chloride, while the aluminum chloride is insoluble to a very high degree in a mixture of hydrochloric acid and ether taken in equal parts and thoroughly saturated with gaseous hydrochloric acid at the atmospheric temperature. We found that 50 c.m.³ of the solution of aluminum chloride, obtained by mixing about 0.1 grm. of the hydrous chloride (dissolved in 2 c.m.³ of water) with the mixture of pure, specially prepared aqueous hydrochloric acid and ether in equal parts, and again saturating the liquid at 15° C. with gaseous hydrochloric acid, left upon evaporation and ignition 0.0004 grm. in each of two experiments—results which indicate a maximum solubility corresponding to 1 part of the oxide or approximately 5 parts of the chloride in 125,000 parts of the equal mixture of ether and aqueous hydrochloric acid of full strength.

Pure aqueous hydrochloric acid of full strength mixes perfectly with its own volume of anhydrous ether, but it is a curious fact that the addition to this mixture of any very considerable amounts of a solution of ferric chloride in strong hydrochloric acid determines the separation of a greenish oily ethereal solution of the ferric salt upon the surface of the acid. The addition of more aqueous acid does not change the conditions essentially, but more ether renders the acid and the oily solution completely miscible. The ferric chloride seems to abstract ether from the ether-acid mixture and, then dissolved in the ether, remains to some extent immiscible with the aqueous acid thus left until the addition of more ether restores to the mixture that which was taken from it by the ferric chloride. Our experiments show that, while for the separation of insoluble aluminum chloride from certain small amounts of soluble ferric chloride, the mixture of the strongest aqueous hydrochloric acid and ether in equal parts serves a most excellent purpose, when larger amounts of ferric chloride are to be dissolved ether must be added proportionately in order to prevent the separation of the ethereal solution of ferric chloride from the rest of the liquid.

Great care was taken to insure the purity of the aluminum chloride used in the test experiments. The so-called pure chloride of commerce was dissolved in the least possible amount of water, and this solution was treated with a large volume of strong hydrochloric acid.

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. ii, Fourth Series, December, 1896.

The chloride thus obtained, free from iron, but possibly contaminated (as we found by experience) with some alkaline chloride, was dissolved in water and converted by ammonia to the form of the hydroxide, which was thoroughly washed and dissolved in hot hydrochloric acid of half-strength. From this solution, after cooling, gaseous hydrochloric acid precipitated the hydrous chloride in pure condition. The chloride thus prepared was dissolved in water, and the strength of the solution was determined by precipitating the hydroxide from definite portions, and weighing the ignited oxide in the usual manner.

TABLE I.

	Al ₂ O ₃ taken in solution as the chloride. Grm.	Al ₂ O ₃ found. Grm.	Final volume. C.m. ³ .	Error. Grm.
1.	0.0761	0.0746	50	0.0015—
2.	0.0761	0.0745	50	0.0016—
3.	0.0761	0.0741	50	0.0020—
4.	0.0761	0.0734	50	0.0027—
5.	0.0761	0.0756	50	0.0005—
6.	0.0157	0.0149	45	0.0008—
7.	0.0157	0.0147	40	0.0010—
8.	0.0157	0.0144	45	0.0013—
9.	0.0480	0.0481	30	0.0001+
10.	0.0960	0.0957	30	0.0003—

In the experiments recorded in Table I., measured portions of the standardised solution were submitted to the treatment with hydrochloric acid and ether. The essential thing in the process is to have at the end a mixture of the strongest aqueous hydrochloric acid with an equal volume of anhydrous ether saturated at a temperature of about 15° C. The most convenient way to secure these conditions seems to be to mix the aqueous solution of the aluminum salt with a suitable volume of the strongest aqueous hydrochloric acid—enough to make the entire volume something between 15 and 25 c.m.³—to saturate this mixture with gaseous hydrochloric acid, while the liquid is kept cool by immersing the receptacle containing it in a current of running water, to intermix a volume of ether equal to the volume of the liquid, and finally, to treat the ethereal mixture once more with the gaseous acid to insure saturation. The precipitated crystalline chloride was collected upon asbestos in a perforated crucible, washed with a previously prepared mixture of hydrochloric acid and ether carefully saturated with the gaseous acid at 15° C., and either ignited after careful drying at 150° or re-dissolved in water, converted to the hydroxide by ammonia in the usual way and weighed as the oxide after filtration, washing, and ignition. In Experiments 1 to 4 the precipitated chloride was ignited directly; in Experiment 5 the ignition was made with great care in an atmosphere of superheated steam; and in Experiments 6 to 10 the chloride was dissolved, precipitated as the hydroxide, and weighed as the oxide.

The experiments in which the chloride was converted to the hydroxide before ignition show upon the average an absolute loss of about 0.0006 gm.; the single experiment in which the ignition took place in steam shows about the same loss—0.0005 gm.; while in those experiments in which the chloride was dried and then ignited directly, the average loss amounts to about 0.0020 gm. The error of the process which involves the precipitation of the aluminum as the hydroxide, falls within reasonable limits, but is plain that the direct ignition of the chloride is liable to error, which may possibly be explicable as a mechanical loss occasioned by the too rapid evolution of the hydrochloric acid and water of crystallisation, or, possibly, as the result of a very slight volatilisation of the aluminum still holding chlorine in spite of the decomposing action of the water upon the chloride. In either case, it would seem to be reasonable to suppose that a layer of some easily volatilisable oxidiser placed upon the aluminum chloride might serve to obviate the diffi-

culty—in the one case, by serving as a screen to diminish mechanical transportation of the non-volatile material; and in the other, by acting as an agent to promote the exchange of chlorine for oxygen on the part of the aluminum chloride.

We have tried, therefore, the expedient of covering the aluminum chloride before ignition with a layer of mercuric oxide, which of itself left no appreciable residue when it volatilised. The hydrous chloride was collected as usual upon the asbestos in a perforated crucible, dried for a half-hour at 150° C. covered with about 1 gm. of the pure mercuric oxide, gently heated with great care under a suitable ventilating flue, and finally ignited over the blast. The results are given below:—

TABLE II.

	Al ₂ O ₃ taken in solution as the chloride. Grm.	Al ₂ O ₃ found by ignition with HgO. Grm.	Final volume. C.m. ³ .	Error. Grm.
1.	0.0761	0.0758	25	0.0003—
2.	0.0761	0.0754	25	0.0007—
3.	0.0761	0.0751	25	0.0010—

It is obvious, therefore, that the precipitation of the crystalline hydrous aluminum chloride from solutions of the pure salt is perfectly feasible and very complete, when effected by aqueous hydrochloric acid and ether thoroughly saturated with the gaseous acid and kept cool; and that the conversion of the chloride into the weighable form of the oxide is best effected by ignition under a layer of mercuric oxide, or by dissolving it in water and precipitating it as the hydroxide, to be afterward washed, dried, and ignited. Of the two methods the former is by far the more convenient.

The precipitation of the aluminum chloride in pure condition from solutions containing ferric chloride ought not, it would seem, to present any difficulty, providing only that the precaution is taken to have present a sufficient excess of ether. The question was put to the test of experiment with the results recorded in Table III.

Measured portions of the standardised solution of aluminum chloride were evaporated nearly to dryness in a platinum dish, an amount of pure ferric chloride equivalent to about 0.15 gm. of the oxide was added in a very little water, 15 c.m.³ of the mixture of strong hydrochloric acid and ether in equal parts were introduced, the liquid was saturated at 15° C. with gaseous hydrochloric acid (the dish being held in a convenient device for cooling it by running water), 5 c.m.³ more of ether were added to secure complete miscibility of the solutions, and more gas passed to perfect saturation. The aluminum chloride was collected upon asbestos in a perforated crucible, washed with a mixture of ether and aqueous hydrochloric acid thoroughly saturated with the gaseous acid, dried at 150° C. for a half-hour, covered with 1 gm. of pure mercuric oxide, and ignited at first gently, and finally over the blast.

TABLE III.

	Al ₂ O ₃ taken in solution as the chloride. Grm.	Al ₂ O ₃ found by ignition with HgO. Grm.	Fe ₂ O ₃ present as chloride. Grm.	Final volume. C.m. ³ .	Error. Grm.
1.	0.0761	0.0757	0.15	25—30	0.0004—
2.	0.0761	0.0756	0.15	25—30	0.0005—
3.	0.0761	0.0755	0.15	25—30	0.0006—
4.	0.0761	0.0755	0.15	25—30	0.0006—

The results show plainly a very satisfactory limit of error.

Determination of the Colouring Power of Litmus.—E. Dieterich (*Helphenberg Annalen*).—The author grinds up 5 grms. of the specimen with 80 c.c. of water, rinses into a 100 c.c. flask, digests at 50° for two hours, lets cool, and filters after settling. 0.05 c.c. of the filtrate, diluted with 100 c.c. of water, must appear distinctly coloured if viewed from above in a stratum of 20 c.m. in thickness.

THE PERMEABILITY OF VARIOUS
ELEMENTS TO THE RÖNTGEN RAYS.

By JOHN WADDELL, B.Sc. (Lond.), Ph.D. (Heidelberg),
Professor of Chemistry, Royal Military College of Canada.

THE following experiments were undertaken with the object of ascertaining whether fluorescent substances are specially opaque to the X rays, in accordance with the well-known laws of absorption illustrated by the Fraunhofer lines in the spectrum.

The investigation thus begun was extended to a number of substances whose permeability to the rays was tested, in order to discover whether any law of general application were apparent.

Barium platinocyanide, thinly laid on paper, was first photographed, and found to hinder the transmission of the rays, and the degree of opacity was sensibly the same whether the fluorescent substance was in direct contact with the photographic film or separated from it by several thicknesses of paper. This experiment was tried shortly after Röntgen's discovery was announced; it was known, however, that platinum was opaque, and that barium was also probably opaque.

A number of substances—some fluorescent, others not—were then taken in the form of powder, made into heaps of about the same thickness, and exposed to the rays. Uranic acid, uranic nitrate, tungstic acid, molybdic acid, sulphate of quinine, barium nitrate, and potassium nitrate were thus photographed on one plate. The sulphate of quinine was apparently perfectly transparent, as no trace of its presence was seen when the negative was developed; the other substances appeared about equally opaque.

As it seemed that fluorescence had little influence one way or the other, the investigation turned chiefly to a comparison of similar compounds of different metals. At first equal weights—0.2 grm.—of substance, in small cylindrical pasteboard pill-boxes, were worked with, but no very definite result was arrived at except that magnesium carbonate was much more transparent than any of the other substances, being comparable in this respect with many organic bodies. Such small quantities of powders were not easily spread in layers of uniform thickness, and thus the photographs were blotched.

From this time on one of Newton and Co.'s focus tubes was used and larger quantities of substances were used, and the time of exposure varied from fifteen seconds to seven minutes.

It had been stated by some observers that the opacity of metals is proportional to their densities, and it would follow from this statement that, if the thicknesses of the metal taken were inversely proportional to their specific gravities, they should be equally opaque.

In my further experiments oxides or carbonates of the opaque element were taken in such quantities that in each box there was 1 grm. or one $\frac{1}{2}$ grm. of the opaque element, which was usually a metal, and which will be so designated in the remainder of this article.

The oxides of molybdenum, tungsten, uranium, silicon, lead, and tin contained 1 grm. of metal; the carbonates of the alkaline earths—because more bulky—were taken in half the proportionate amount.

It was thought that, by varying the lengths of exposure in different experiments, a difference might be detected between the different substances; that with some length of exposure the opacity might show different. With a very short exposure it was possible that some of the substances would allow no appreciable amount of the radiations to pass through, while others would transmit some of the rays. There was very little difference between the different substances as regards the shadow cast on the photographic plate, and this might seem to substantiate the idea that the opacity of the metals is proportional to their densities, except that the carbonates containing $\frac{1}{2}$ a grm. of metal were not noticeably different from the com-

pounds containing a grm. of metal. No conclusions could therefore be drawn from the experiments thus far described.

I have given so full an account of these unsuccessful experiments because I believe that many of the observations recorded have been open to just the kind of uncertainties I have mentioned. Where the metals can be beaten out thin it may be all right to test their opacity in a manner similar to the above, but in other cases the result is misleading.

All of the above experiments may be regarded as attempts to compare the *opacities* of the different metals, but these are so great that in the short exposure they all appear equal; hence I determined to compare the *transparencies*,—that is, instead of having the photographic plate exposed except when covered by the substances, I protected the sensitive film by a sheet of lead, about an eighth of an inch thick, in which holes were punched small enough to be covered by the boxes containing the powders. I chose for experiment the oxides and carbonates of the various groups of metals—Mo, W, Ur; Si, Sn, Pb; Mg, Zn, Cd; Ca, Sr, Ba; and Li, Na, K.

In addition I took photographs of the carbonates of nickel and cobalt, and of the oxide of copper.

The time of exposure ranged from fifteen minutes to nearly an hour. The weights of the lithium, sodium, and potassium carbonates used contained 0.5 grm. of metal, because the larger quantity could not be put in the boxes; they were compared with calcium carbonate, which also contained 0.5 grm. of metal, while double the amount of calcium carbonate in another box was compared with the other compounds which also contained a grm. of the metal. There was very little difference between the lithium and sodium carbonates, which were much more transparent than the potassium carbonate, while this last was of appreciably the same transparency as the calcium carbonate containing the same amount of metal.

In the next group the calcium carbonate was much more permeable than the strontium or barium carbonates,—so much so that I thought the permeability of the calcium and barium might be inversely proportional to the atomic weights; I therefore compared the permeability of a quantity of barium carbonate containing $\frac{1}{2}$ grm. of barium with that of a quantity of calcium carbonate containing 1 grm. of calcium, and found the former greater than the latter, so that the idea suggested above had to be abandoned. In any case such a relationship between the metals could have been accidental only, since strontium carbonate is no more permeable than barium carbonate.

Zinc carbonate was slightly more permeable than the barium carbonate, and naturally far inferior in transparency to magnesium carbonate. Cadmium oxide was a little less permeable than the zinc compound, and about equal to tungstic acid (WO_3), which was if anything a shade more permeable than the corresponding compounds of molybdenum and uranium, containing the same amount of metal. In all of these cases, however, the photographic effect was slight, and was visible on the negative only when held in a favourable position.

In the group which consisted of silicon, tin, and lead, it was found that the oxide of the first member was far more permeable than that of either of the others, which were more nearly alike and approached much nearer the other heavy metals.

Nickel and cobalt carbonates and copper oxide are as nearly as possible equal to tungstic acid.

As the result of the above experiments, it is evident that there is no universal connection between the density of the metal and its opacity, because lithium and sodium carbonates are both much more permeable than potassium carbonate, while the specific gravity of potassium is between that of lithium and sodium. On the other hand, it is not in proportion to the atomic weight, for sodium carbonate is not less, but slightly more, permeable than lithium carbonate, as well as much more permeable than potassium

carbonate. In the same way strontium carbonate is not midway between calcium and barium carbonates.

With the heavier metals the opacity seems to be nearly in proportion to the density, but for those metals that cannot be obtained in very thin plates it is difficult to speak with certainty, since they are all so opaque.

It was because the metals themselves could in many cases not be experimented with that I had used the oxides and carbonates, but I tested the permeability of potassium, sodium, magnesium, and aluminium.

The two alkali metals were enclosed in paraffin wax, and were 3·9 m.m. thick; the aluminium and magnesium were 1·5 m.m. thick. The magnesium was more permeable than the aluminium, and much more permeable than the potassium, though not so permeable as the sodium. There was nearly the same relation between the opacities of the potassium and sodium in the metallic state and in the form of carbonate.

In one of the experiments described above the permeability of calcium fluoride was compared with that of calcium carbonate containing the same amount of metal, and found to be about equal to it. This was a still more conclusive proof that fluorescence does not increase the impermeability of the substance. The fact, moreover, suggested to me that all the permeable elements had proved to be of low atomic weights.

I therefore decided to compare fluorine with chlorine, bromine, and iodine; and for that purpose used the sodium salts, and took quantities containing $\frac{1}{2}$ a gram. of the halogen. The advantage of the sodium salt was that sodium had proved to be tolerably permeable, and I was at all events certain that, if the fluoride proved to be more transparent than the other salts, fluorine must be still more transparent than the other halogens, because it contained so much greater quantity of metal. Sodium fluoride contains more sodium than fluorine, while sodium iodide does not contain one-fifth as much.

On the same photographic plate I had boracic acid containing $\frac{1}{2}$ a gram. of boron, and a piece of sheet aluminium whose weight for the same cross section was one-third of a gram.

Unfortunately in this experiment I did not have the same induction-coil as before, but was compelled to use a much smaller one giving a spark of less than $\frac{1}{2}$ an inch in length, and, though I gave an exposure of over four hours, the chloride, bromide, and iodide did not permit of any photographic effect on the sensitive film. I am therefore unable to say whether there would have been any difference shown between these salts if I had had a more powerful coil; but it was clearly demonstrated that fluorine is more permeable than the other halogens, because the photographic effect through over a gram. of the sodium fluoride (corresponding to 0·5 gram. of fluorine) was only a little inferior to that through one-third of a gram. of aluminium. I may add that quite a perceptible effect was produced by the radiations passing through copper foil about 0·05 m.m. in thickness.

The boracic acid was not so permeable as the sodium fluoride. The total weight of the former was over twice as much as that of the latter; and it is quite possible that part of the opacity was due to the oxygen, and that the permeability of boron is greater than appeared in the experiment, and probably superior to that of aluminium.

I have not tried the permeability of beryllium; but Capt. Cochrane (Instructor in Physical Science in the Royal Military College of Canada), in the course of an investigation on the relative permeability of real and imitation gems, found that beryl is transparent. All of the real gems thus tested, with the exception of garnet, were quite permeable, and garnet was the only one containing a heavy metal (iron).

Though, in the experiment spoken of a few sentences back, the radiations were not effective through sodium chloride, I had in one of the earlier experiments a crystal of halite of same cross section as calcium carbonate powder in the box. The halite weighed 1·5 grms. and the

calcium carbonate 1·25 grms., and the permeability was almost exactly equal. Of the halite the more opaque element is the chlorine, and it seems to be more permeable than calcium or potassium.

On the same negative, the transparency of a selenite crystal weighing 0·85 gm. was considerably greater than that of the calcium carbonate, and as closely as I could judge it was about equal to that of the same amount of carbonate. The proportion of calcium in selenite is less than in calcium carbonate, and therefore part at least of the opacity is contributed by the sulphur; but probably the latter is more permeable than chlorine.

I give these data because I have not now at hand the apparatus for making the more decisive test, which would be to compare the permeability of sulphur with that of aluminium on the one hand and of sodium chloride on the other.

The experiments I have described make it evident that the elements may be divided, so far as permeability is concerned, into two classes,—those of low atomic weight and those of higher atomic weight,—the transition taking place between the atomic weights 30 and 40. Among the higher elements the opacity is probably not far from being proportional to density, but with the elements of low atomic weight the same law does not hold; sodium, for instance, is decidedly more permeable than aluminium, because in the experiment above mentioned the thicknesses of the two metals were approximately inversely as their densities. Lithium and sodium are more nearly alike.

Metals and non-metals cannot be differentiated from each other; boron is less permeable than sodium, and sodium is less permeable than oxygen.

One is naturally led to speculate as to the reason of the greater permeability of substances of low atomic weight. Until our knowledge of the phenomena connected with Röntgen rays is more definite, hypotheses must be vague; but the suggestion readily occurs to one that the atoms of low weight are simpler in structure, and impede the motions of the ether to a less extent than do the atoms of high weight. This, on the assumption that the ether is the medium of transmission of the Röntgen radiation. If, however, matter be the vehicle of transmission of energy, the transparency may be due to the greater ease with which atoms of small weight are set in motion.

Addenda.—In comparing the relative permeability of crystals and the same mineral powdered, I found that the photograph of the latter, though otherwise similar to that of the former, showed a granulated appearance. This was also the case with many of the powders. I thought that it might be due to the powder being in little more or less coherent lumps; but precipitated silica, which had such a thickness that more than 2 grms. of it were in the little box,—a thickness of, say, three-quarters of an inch,—showed the same granulation.

The calcium carbonate did not exhibit it, however, nor did the zinc carbonate or sodium carbonate.

I do not know whether the idea has been universally abandoned, that the photographic effect is due to the fluorescence of the Crookes tube; but the fact that when the sensitive plate is exposed to the rays from different sides of the tube the photographic effect is vastly different seems to me fatal to such an hypothesis. When, with the focus tube, the plate is so situated that *light*, starting from the cathode and reflected by the anode, would be reflected to the plate, the photographic effect is far greater than if the tube is rotated into any other position, say at right angles to the former one. A similar phenomenon is shown if the tube be used to discharge a gold-leaf electroscope. This is not due to difference of distance from the most fluorescent part of the tube; nor is it due to the radiations going through more glass when the Crookes tube is inverted. I have taken photographs through two thicknesses of glass, in the ordinary dry plates, and have found them quite distinct.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 3rd, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. James Herbert Brown, Dallas Place, Lancaster; John Wallis Dodgson, B.Sc., 47, Hirwain Road, Aberdare, Glamorgan; Lawrence Dufty, 33, Broomhall Place, Sheffield; Joseph Lake Gibbons, West Carlton Street, Blyth; Alexander William Gilbody, M.Sc., Ph.D., Owens College, Manchester; Harold Walter Gough, B.A., 73, Billing Road, Northampton; Ernald George Justinian Hartley, B.A., Wheaton Aston Hall, Stafford; Charles Henry Martin, 14 Aldred Street Crescent, Salford; William James Stainer, B.A., 3, Havelock Road, Stanford Avenue, Brighton; Samuel Matthew Walford, 62, Bloom Street, Stockport; James Wallace Walker, M.A., Ph.D., University College, London.

The following were duly elected Fellows of the Society: Henry Edward Aykroyd, William Ballingall, M.A., Gopal Chandra Bauerfee, Charles Bathurst, B.A., Lauritz Hansen Bay, Charles Edward Browne, B.Sc., Walter William Cobb, M.A., George Harold Cross, B.Sc., William Duncan, Walter John Elliott, M.A., Eric David Ewen, John Thomas Fleet, George George, Arthur Croft Hill, B.A., Charles Alexander Hill, John William Hinchley, William Trevor Lawrence, B.A., Robert Dexter Littlefield, Thomas Henry Lloyd, Thomas William Lockwood, Hugh Manners, M.A., B.Sc., Edward Seaborn Marks, Arthur Stanley Mayfield, William M. Miller, Landon Clarence Moore, Francis Ambrose Moss, Herbert William Moss, Joseph Terrence de la Mothe, Alexander Henry Mitchell Muter, William Harrison Pearsall, Henry William Potts, Frederick Belding Power, Ph.D., William Russell, Arthur Edwin Saville, Herbert Cecil Seabrooke, Kotaro Shimomura, B.Sc., William Horace Sodeau, B.Sc., Charles Thompson, B.Sc., William Henry Walker, William Watson, M.A., Edwin Whitfield Wheelwright, B.A., Ph.D., John Inctus Whimster, John Harrison Wigner, Ph.D., Alfred James Wilcox.

Of the following papers those marked * were read:—

*156. "Constitution and Colour." By ARTHUR G. GREEN.

In a scheme for the qualitative analysis of the coal-tar colouring-matters published in 1893 (*J. Soc. Chem. Ind.*, 1893, xii., 3), the author pointed out that the leuco-compounds of various dye-stuffs exhibit a striking difference of behaviour on exposure to air. Leaving out of account those which are completely split up by reduction (viz., azo-, nitro-, and nitroso-colours), it is possible, by means of this reaction, to classify colouring-matters into two groups, viz.:—I. Colours whose leuco-compounds are not easily re-oxidised on exposure to air. II. Colours whose leuco-compounds are rapidly re-oxidised on exposure to air.

Group I. comprises all the colouring-matters of the triphenyl-methane series, the phthaleins or pyrone colours, indophenols, and indamines. Group II. comprises the indigo class, the azines, azonium colours, oxazines, thiazines, acridine colours, thiazol colours, quinoline colours, oxyanthraquinone colours, and certain colouring-matters of unknown constitution.

In explanation of the cause underlying this difference of behaviour, the author, in 1892, put forward the suggestion (*Proc.*, 1892, viii., 195) that, assuming the correctness of the "quinonoid" theory of colour (Armstrong (*Proc.*, 1888, iv., 27; 1892, viii., 101, 143, 189, and 194; 1893, ix., 52 and 206), the colouring-matters of the first group might be regarded as *para*-quinonoid,—



of the second group as *ortho*-quinonoid,—



In the present paper this view is more fully discussed, and further evidence is brought forward in confirmation of it.

An examination of the members of the two groups shows that, whilst nearly all the colouring-matters of Group I. are compounds substituted in the para-position alone, no plain para-substituted compounds are found in Group II.; on the other hand, whilst Group II. contains compounds substituted in the ortho-position alone (e.g., indigo) and compounds substituted in both positions, no plain ortho-substituted compounds are to be found in Group I. Therefore, if the "quinonoid" theory of colour be accepted, it follows that dye stuffs, which, from their constitution, must be ortho-quinonoid, only occur in Group II., whilst those which must be para-quinonoid, only occur in Group I.

In Group I. the theory agrees in all cases with the usually accepted constitution of the colours. In Group II., when it is not in accord with the usually accepted view, the ortho-quinonoid formulæ give as good, or better, interpretations to the properties of the colouring-matters than the para-quinonoid formulæ previously assigned them.

It would be anticipated, from the well-known interrelationship of ortho-substituents, that two groups occurring in an ortho-position to each other would have a greater tendency to enter into a more intimate union, and therefore would be more oxidisable than if they stood in the para-position.

The stability towards acids of the colouring-matters of the methylene-blue and safranin series, and the oxidisability of their leuco-compounds, compared with the extreme instability to acids of the parent indamines (paraquinone-imides) and non-oxidisability of their leuco-compounds, forcibly suggest a change of type.

The tendency exhibited by many azines and oxazines to form amido-derivatives by addition, as in the case of Meldola's blue, can only receive an explanation by the assumption of an ortho-quinonoid structure, since, in the naphthalene nucleus, where the substitution takes place, a para-quinonoid structure is not possible.

DISCUSSION.

Dr. KIPPING said that Mr. Green's classification of certain dye-stuffs into derivatives of ortho- and of paraquinones respectively, being based solely upon the rapidity with which the corresponding leuco-compounds undergo aerial oxidation, it would add to the interest of his communication if he could define more exactly the words "easily oxidised" by introducing the element of time; for the rapidity of oxidation of all the leuco-compounds of one class would probably not be the same, and consequently those reduction products of paraquinones which oxidised most easily might do so more rapidly than the leuco-compounds of some of the orthoquinones. Should this never, or rarely, occur, Mr. Green's classification would be extremely useful; but as it does not even include all dye-stuffs, it cannot be regarded as affording any support to the view held by Dr. Armstrong, namely, that all coloured carbon compounds have a quinonoid structure. This view, attractive though it may be, and supported by the numerous examples which have been brought under notice, is nevertheless untenable: that all quinones and their derivatives are coloured may be true, but to assume that all coloured substances are quinones would necessitate in many cases the adoption of constitutional formulæ utterly at variance with chemical facts. Without discussing the meaning of the somewhat vague word "colour," it may be pointed out that the colour of a substance depends, amongst other conditions, on its crystalline structure. In the course of some work carried out with Mr. Revis, it was noticed that isonitrosohydriindone

forms a yellow sodium derivative, the colour of which depends on the temperature at which it is crystallised; when heated at 70–80° the yellow salt is rapidly converted into a scarlet modification, owing to a change in crystalline form taking place. Numerous examples of a similar kind are known, and taking this fact into consideration, and having regard more especially to the number of undoubted exceptions to Dr. Armstrong's colour rule, it is impossible to accept his generalisation in its present form.

Mr. LING agreed in considering that the quinone theory was not established as a general rule.

Dr. ARMSTRONG thought that Mr. Green's generalisation was of considerable value as a working hypothesis, but he was inclined to doubt whether it would be possible by means of such a test as that suggested to sharply divide dye-stuffs into two classes; it was rather to be expected that the members of the two classes would merge gradually into each other. As the method would in many cases incite the further investigation of structure, which was so much to be desired, it must prove to be of considerable service. As to the alternative formulæ suggested by Mr. Green, he could not regard them as satisfactory on the whole; the representation of oxygen as a tetrad in such a case as that of Meldola's blue, for example, appeared to him to involve conclusions beyond the bounds of probability. Mr. Green had spoken of the Armstrong-Nietzki quinonoid theory of colour: unaccustomed as he was to put forward claims of priority, he could not help remarking that although Nietzki had undoubtedly called attention to the occurrence of quinonoid structure in many colouring-matters, he had never attempted to generalise. He, the speaker, had, however, endeavoured to extend the hypothesis not only to colouring-matters, but to coloured substances generally, and had given a definition of the term quinonoid, which included even substances such as iodoform. No doubt the difficulties to be overcome were very great, and it would be long before we should be able to explain all cases of the occurrence of colour; meanwhile all we could do was to patiently investigate the facts.

Mr. GREEN, in reply, wished it to be understood that he regarded the quinone theory as affording a satisfactory explanation of the colour of organic dye-stuffs, though not of the colour of all coloured organic compounds.

*157. "Derivatives of α -Hydrindone." By C. REVIS and F. STANLEY KIPPING, Ph.D., D.Sc.

As α -hydrindone and camphor are in some respects analogous to constitution (inasmuch as each contains two closed carbon chains, in one of which occurs the group $-\text{CH}_2\text{CO}-$), the behaviour of the two ketones and of corresponding derivatives has been studied, in order to ascertain to what extent they would show analogous reactions; it has thus been found that, except in a few instances, there is a marked difference in chemical behaviour.

α -Hydrindoneoxime, for example, behaves quite unlike camphoroxime when heated with mineral acids, as it yields the two condensation products (anhydrosihydrindone and truxene) which are produced from hydrindone itself (Kipping, *Trans.*, 1894, lxx., 480). Monobromohydrindone, unlike α -bromocamphor, is readily acted on by alcoholic potash, giving a condensation product of the composition $\text{C}_{18}\text{H}_{13}\text{BrO}_2$ (*Proc.*, 1895, x., 157). Dibromohydrindone resembles α -dibromocamphor in withstanding the action of nitric acid, but it differs from the camphor derivative in being readily acted on by alcoholic potash, giving a condensation product of the composition $\text{C}_{18}\text{H}_{11}\text{BrO}_2$; this substance crystallises from benzene in flat prisms, which contain 1 molecule of benzene, and melts at about 150°, also decomposing. A somewhat similar condensation product is obtained by treating dibromohydrindone with an alcoholic solution of sodium ethoxide; this compound crystallises in prisms melting

and decomposing at 173–174°, and probably has the composition $\text{C}_{18}\text{H}_{10}\text{O}_2\text{Br}\cdot\text{OEt}$.

Attempts to prepare hydrindene, C_9H_{10} , by first reducing hydrindoneoxime to the primary amine, $\text{C}_9\text{H}_9\cdot\text{NH}_2$, and then converting the base into the hydrocarbon by the ordinary methods, were not more successful than those previously made by König (*Inaug. Diss.*, Leipzig, 1889), owing to the production of resinous compounds in the various stages of the process.

Benzoylaminohydrindene, $\text{C}_9\text{H}_9\cdot\text{NH}\cdot\text{COPh}$, prepared from the base, crystallises in colourless needles, and melts at 142–143°.

Benzylideneaminohydrindene, $\text{C}_9\text{H}_9\cdot\text{N}:\text{CHPh}$, the condensation product of benzaldehyde and aminohydrindene, forms transparent prisms, melting at 74–75°.

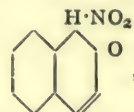
Aminohydrindeneoxalate crystallises in clusters of white opaque prisms, and is rather sparingly soluble in cold methyl alcohol and in cold water.

Hydrindone semicarbazide, $\text{C}_9\text{H}_8\cdot\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, separates from dilute acetic acid in prisms, which contain 7 mols. of water; it melts and decomposes at about 239°.

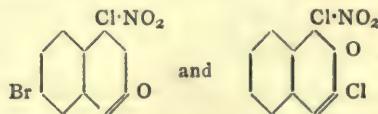
*158. "Notes on Nitration." By HENRY E. ARMSTRONG.

In previous notes on nitration (*Proc.*, 1891, vii., 87–91), E. C. Rossiter and the author have drawn attention to the part played by keto-compounds, and to the explanation which their formation, as well as that of other addition compounds, affords of the production of secondary products in nitrations.

Attention is now drawn to the conditions to be observed in preparing normal products of nitration. However carefully β -naphthol be subjected to the action of nitric acid, a considerable proportion of resin is always formed, even when the product is subjected to the action of reducing agents; but if bromo- β -naphthol be used instead, the formation of resin may be entirely avoided, a practically theoretical yield of 1 : 2-nitro- β -naphthol being obtained. Obviously, in the latter case, the addition compound which is first formed, and also the keto-compound derived from it, are far less sensitive to the action of the unchanged naphthol, so that the interaction affording the resin is prevented from occurring. Moreover, although a nitro-keto-compound, such as is represented by the formula—



would not be converted by reduction into nitronaphthol, it is to be expected that if bromine occupied the place of the hydrogen, it would be readily removable. Not only is this actually the case, but nothing more powerful than a sulphite is needed; yet, in some instances, it is necessary to use a stronger reducing agent; thus, the compounds—



are unaffected by sulphite, but as experiments made by Mr. E. Rich show, they are at once converted into the corresponding nitronaphthols by means of hydrogen iodide.

*159. "3'-Bromo- β -naphthol." By HENRY E. ARMSTRONG and W. A. DAVIS.

At present, the only bromo- β -naphthol known is the 1 : 2-modification, which is the sole product of the direct interaction of bromine and the naphthol; indirect methods capable of affording isomeric forms are much needed. The authors have succeeded in devising a method of converting 1 : 3'-dibromo- β -naphthol into 3'-bromo- β -

naphthol by removing the bromine atom in position 1; this consists in digesting the dibromo-compound with a saturated solution of hydrogen iodide, ultimately at a temperature not exceeding 65°. If care be taken, the yield is that indicated by theory; but if the naphthol be allowed to dissolve in the acid solution, and the temperature to rise too high, an intractable condensation product is alone obtained.

3'-Bromo- β -naphthol crystallises from benzene in colourless needles melting at 127°; the acetate derived from it melts at 103°.

On sulphonation by means of cold sulphuric acid, it yields a somewhat unstable monosulphonic acid, which is converted into 1:3'-dibromo- β -naphthol by bromine, and into 1-nitro-3'-bromo- β -naphthol by nitric acid; doubtless, therefore, sulphonation takes place in position 1.

By heating the bromonaphthol with excess of sulphuric acid at 100°, a stable disulphonic acid is produced.

The behaviour of higher brominated derivatives of β -naphthol and of the bromo- α -naphthols with hydrogen iodide will be considered in a subsequent communication.

*160. "Derivatives of Nitro- β -naphthols." By W. A. DAVIS.

The difficulties which attend the nitration of β -naphthol do not affect that of its ethers, which show no tendency to give keto-compounds; moreover, the nitromethoxy- and nitroethoxy-naphthalenes are all more or less intensely coloured substances, whereas the corresponding phenol derivatives are colourless; hence the investigation of these compounds is of importance from several points of view.

Besides repeating and confirming Gaess's observations on the nitration of β -ethoxynaphthalene (*Z. pr. Chem.*, [2], 43), the author has prepared the methoxy-compounds corresponding to those described by Gaess, and has subjected both series to crystallographic examination. 1:2-Nitromethoxynaphthalene (m. p. 126°) is the main product when nitration is effected in acetic acid solution at a temperature not exceeding 15°; it forms 90 per cent of the total product, and is accompanied by about 1 per cent of the 1':2-nitromethoxy- (m. p. 69°) and about 3 per cent of the 3':2-nitromethoxy-compound (m. p. 134°).

The amido-derivatives were prepared by reducing the nitro-compounds with tin and hydrochloric acid. 1:2-Amidomethoxynaphthalene melts at 84°, and its acetyl derivative at 175°; the 3':2-amido-compound melts at 98°, and its acetyl derivative at 183°, whilst 1':2-acetamidomethoxynaphthalene melts at 145°.

The action of a molecular proportion of bromine on 1:2-nitroethoxynaphthalene gave 3':1:2-bromonitroethoxynaphthalene (m. p. 141°), the structure of which was determined by its formation on ethylating 3':1:2-bromonitronaphthol. When hydrolysed by alcoholic potash, it yields 3':1:2-bromonitronaphthol (m. p. 122°).

If any excess of bromine be used in the bromination, dibromomethoxynaphthalene (m. p. 94°) and tribromomethoxynaphthalene (m. p. 128°) are formed by the displacement of the NO₂ group by bromine.

3':1:2-Bromamidomethoxynaphthalene melts at 84°, and its acetyl derivative at 246°.

3':1:2-Bromonitromethoxynaphthalene, prepared by brominating 1:2-nitromethoxynaphthalene, melts at 152°; the corresponding amido-compound melts at 73°, and its acetyl derivative at 252°. 3':1:2-Bromonitronaphthylamine, obtained by heating 3':1:2-bromonitroethoxy- or methoxynaphthalene, with alcoholic ammonia at 160°, is a yellow, crystalline substance, melting at 190°.

On nitrating 1:2-nitromethoxynaphthalene with concentrated acid (*d* 1.42) at 0°, a mixture of 1:3':2 and 1:1':2-dinitromethoxynaphthalenes was obtained; these were separated only with difficulty. 1:3':2-Dinitromethoxynaphthalene was, however, obtained in a pure state by nitrating 1:3'-nitromethoxynaphthalene at 0°. It melts at 198°. The 1:1':2-dinitro-compound melting at

190° was obtained by similarly nitrating 1:1'-nitromethoxynaphthalene. The structure of these two dinitro-compounds was determined by converting them into the corresponding dinitronaphthylamines, which had been previously prepared and described by Gaess (*loc. cit.*).

1:2-Nitromethoxynaphthalene, on being heated with alcoholic potash, easily yields 1:2-nitronaphthol; on being heated with alcoholic ammonia at 160°, it is converted into 1:2-nitronaphthylamine. It is noteworthy that, under similar conditions, 1:2-nitronaphthol yields scarcely any nitronaphthylamine, a large amount of resin being formed.

SO₂Cl₂ is apparently without action on 1:2-nitroethoxy- or nitromethoxynaphthalene; it acts, however, very readily on 1:2-acetamidomethoxynaphthalene, giving a beautifully crystalline monochloro-derivative, melting at 167°. The structure of this has not yet been determined. In order to determine whether β -ethoxy- α -naphthylamine resembles β -naphthol or α -naphthylamine, the behaviour of its acetyl compound with bromine was studied; the action was carried out at 0°. 3':1:2-Bromacetamidomethoxynaphthalene, m. p. 245°, was obtained as sole product. Thus its behaviour is simply that of a derivative of β -naphthol in which position 1 is occupied, the NHAc group, apparently, being without influence; this is of especial interest, as, according to a private communication from Professor Nietzki to Professor Armstrong, its behaviour towards nitric acid is comparable with that of α -acetnaphthalide.

The behaviour of bromine with β -methoxy- α -acetnaphthalide is the same as towards the ethoxy-compound, 3':1:2-bromomethoxyacetnaphthalide (m. p. 252°) being obtained.

*161. "Morphotropic Relations of β -Naphthol Derivatives." By W. A. DAVIS.

Although the crystallographic relationships of benzene derivatives have been very fully investigated, little work of a similar character has been hitherto carried out upon naphthalene compounds, and only one morphotropic series of derivatives has been recognised, viz., that afforded by the chloro- and bromo-naphthalenetetrachlorides, which has been discussed by Hintze (*Pogg. Ann.*, 1874, vii., 177). The author has examined the compounds referred to in the previous note, and finds the following crystallographic constants.

Substance.	System.	Geometrical constants.
		$a : b : c$
1:2-Nitronaphthol	Monosymmetric	$1.5755 : 1 : 1.1938$ $\beta = 101^\circ 26'$
1:2-Nitroethoxy-naphthalene	Orthorhombic	$2.4897 : 1 : 1.1606$
1:2-Nitromethoxy-naphthalene	Anorthic	$0.9382 : 1 : 1.2088$ $\alpha = 97^\circ 45', \beta = 92^\circ 8',$ $\gamma = 88^\circ 27\frac{1}{2}'$
1:2-Nitrobenzyl-naphthol (Sayer)	Orthorhombic	$0.4892 : 1 : 1.0532$
1:2-Acetamidomethoxynaphthalene	Monosymmetric	$0.7999 : 1 : 0.7611$ $\beta = 99^\circ 21'$
1:3':2-Nitrobrom-ethoxynaphthalene	Anorthic	$1.4274 : 1 : 1.0265$ $\alpha = 95^\circ 0', \beta = 109^\circ 18',$ $\gamma = 80^\circ 15'$
1:3':2-Dinitromethoxynaphthalene	Orthorhombic	$? : 1 : 1.1526$

The crystallographic data thus obtained afford a series presenting the following salient points:—

(1) In the transitions from 1:2-nitronaphthol to its methyl, ethyl, and benzyl ethers, although marked changes of symmetry occur, the axial ratio $c : b$ remains nearly constant. In the passage from nitro- β -naphthol (mono-

symmetric) to its methyl ether (anorthic), there is a degradation of symmetry; but an increase in symmetry occurs in passing from 1:2-nitronaphthol to its ethyl ether (orthorhombic). These changes of symmetry are analogous to those which occur in the benzene series in passing from acetanilide to methyl and ethyl acetanilide respectively, only in the latter case the changes are not brought into evidence by changes of system, but only by corresponding changes in the axial ratios.

(2) When 1:2-nitroethoxynaphthalene (orthorhombic) is changed by the introduction of a bromine atom into position 3', a degradation to anorthic symmetry takes place, the axial ratio $c:b$ remaining, however, nearly unaffected.

(3) A remarkable increase of symmetry occurs when 1:2-nitromethoxynaphthalene (anorthic) is converted into the 1:3':2-dinitromethylether (orthorhombic), whilst the ratio of the c and b axes remains nearly constant; this increase of symmetry accompanying the introduction of successive units of the same radicle is comparable with the change in symmetry that occurs in the benzene series in passing from paranitrophenol (monosymmetric) to dinitro- and trinitro-phenol, both of which are orthorhombic, the symmetry in the case of the trinitro-compound tending towards that of the tetragonal system. When the various nitro-derivatives are melted on a microscope slide, and the solidified films are examined between crossed nicols, in the manner recently suggested by Mr. Pope (*Proc.*, 1896, xii., 142) the appearances they present are very characteristic, as the photographs which are exhibited show; and an important proof is thus given of the use to which such a method can be put either in identifying isomeric substances occurring together—particularly if these melt at nearly the same temperature and are, therefore, liable to be confused with one another—or in recognising the occurrence of a change from one crystalline modification to another.

*162. "Researches on Tertiary Benzenoid Amines." II. By CLARE DE BRERETON EVANS, B.Sc.

In continuation of the experiments referred to in a previous abstract (*cf. Proc.*, 1896, xii., 235), the behaviour of diethylaniline, as well as that of dimethylortho- and dimethylpara-toluidine, has been further studied, and the series of isomeric dimethylanilinesulphonic acids has been completed by the preparation of the ortho-compound. For purposes of comparison, methyl- and ethyl-aniline have also been subjected to sulphonation.

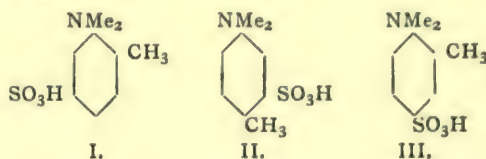
Dimethylanilineorthosulphonic acid was prepared by methylating parabromanilineorthosulphonic acid and subsequently reducing the product.

The constitution of the acids derived from the toluidines was determined by methylating the sulphonic acids of toluidine of known constitution.

Summarising the facts, the striking conclusion has been established that whereas orthosulphonic acids are readily obtained from aniline derivatives—for example, parabromaniline, meta-acids only are formed from dimethyl- and diethylaniline and dimethylparatoluidine; there being, apparently, an extraordinary "aversion" on the part of the sulphonic radicle to take up the ortho-position relatively to the NR_2 group.

A similar inhibiting influence appears to be exercised by the group in preventing the entry of more than one bromine atom into the ortho-position. Such being the case, it is the more remarkable that when the sulpho-group does become displaced bromination extends much further in the case of the tertiary amines: dimethylaniline-para- and ortho-sulphonic acids being converted into tetrabromodimethylaniline and diethylanilinepara-sulphonic acid even into pentabromodimethylaniline; 1:2:5-dimethylorthotoluidinemetasulphonic acid in like manner yields tetrabromodimethylorthotoluidine. Sulphanilic acid, it is well known, yields only tribromaniline.

In the case of the acids derived from the dimethyltoluidines, viz.,—



of which No. III. was prepared by methylating the toluidine sulphonic acid, only the first yields a perbromide.

It is noteworthy that the sulphochlorides of the various acids are all hydrolysed with somewhat unusual readiness.

Methyl- and ethyl-aniline are found to behave exactly as aniline, so that the presence of hydrogen in association with the nitrogen atom would appear to play a part in the formation of orthamido-derivatives.

It is proposed to extend the experiments to the dimethylxylydines and cumidines.

163, "On the Circumstances which affect the Ratio of Solution of Zinc in Dilute Acids, with especial Reference to the Influence of Dissolved Metallic Salts." By JOHN BALL, A.R.S.M.

The author considers the effects on the rate of solution of zinc in dilute acids of (i.) variations of concentration of the acid; (ii.) previous special treatment of the acid; (iii.) variations of temperature; (iv.) variations of pressure; (v.) variations of the surface condition of the zinc; (vi.) alloys of known amounts of foreign metals with the zinc; (vii.) performance of the solution in vessels of different materials; (viii.) addition to the acid solution of (a) oxidising agents; (b) reducing agents; (c) foreign acids; (d) salts of foreign metals.

The main portion of the paper deals with the effects produced by the presence of salts of various metals in the solution. Two main series of quantitative experiments for the comparison of the relative effects of salts of the different metals are described: one in solutions of sulphuric acid with magnesium, aluminium, chromium, manganese, iron, silver, copper, cobalt, or nickel sulphates as added salts; and one in solutions of hydrochloric acid, with manganese, lead, tin, copper, cobalt, gold, platinum, or nickel chlorides added. There is also a separate set of experiments in sulphuric acid solutions, with cobalt sulphate as added salt, in order to determine quantitatively the influence of the amount of salt used.

The metal used was pure distilled zinc, specially cast in very thin sheet. The results show that, both with sulphuric and hydrochloric acids, the addition of the foreign salts always accelerates the reaction, except in the case of magnesium and aluminium salts, which seem to be nearly without influence. The accelerating effect is most felt at the beginning of the reaction, and the velocity soon reaches a maximum (higher than that which would hold if no salt were present), which is practically constant nearly to the end. The acceleration is shown to be governed by a number of causes, of which the amount of metal precipitated from the added salt on the zinc is only a subordinate one, as the acceleration is often very great in cases where no precipitation can be determined—e.g., 0.020 gm. of nickel sulphate is added to a mixture of 17 c.c. of water, with 8 c.c. of sulphuric acid, at a temperature of 40°, increased the maximum velocity of reaction with zinc 37.87 times. In these cases a very minute trace of the added salt exerts an enormous influence, and, as shown by the experiments with cobalt sulphate, the effect of adding more of the salt becomes less perceptible as the total amount is increased, and ultimately we reach a point where further addition is without influence.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, December 11th, 1896.

Prof. AYRTON, Vice-President, in the Chair.

A PAPER on the "*Applications of Physics and Mathematics to Seismology*" was read by Dr. C. CHREE.

Prof. J. Milne has attempted to account for certain changes in the indications of spirit-levels and delicately suspended pendulums by the supposition that they are due to meteorological agencies, such as rainfall or evaporation. Thus he considers that a relative excess of moisture, say, on the west of an observatory, is equivalent to a surface load on that side, tending to make the ground on which the observatory rests slope downwards from east to west. The author, by making the assumptions as to the physical state of the substance of the earth, that it is a homogeneous, isotropic, elastic solid, has examined, in as general manner as possible, the amounts of flexure which would be produced by different systems of loading. He points out that the alteration in the reading of such an instrument as a spirit-level depends, not only on the bending of the surface of the earth, but also on the attraction exerted by the load, which slightly alters the direction of "gravity." He shows that if ψ_1 is the alteration in level produced by the bending, and ψ_2 the alteration in the direction of gravity, then the ratio ψ_1/ψ_2 depends only on the elastic constants of the earth, and is quite independent of the shape and size of the loaded area. In the case of a material having the elasticity of steel, $\psi_1/\psi_2=2$, for brass $\psi_1/\psi_2=5$, and for an incompressible material $\psi_1/\psi_2=11$. The author considers that this last value most truly represents what occurs in practice, and hence that the pressure effect is considerably larger than the gravitational effect. The pressure effect is worked out for the cases where the loaded area is a square, and a long narrow rectangle, and it is found that for a square of 100 metres side the effect, at a point 1 metre from one side, of loading the square with a layer of water 1 c.m. thick is to alter the level by 0.0012 seconds of arc. For the case of a tidal river 100 yards wide, and for a rise of 5 metres, the effect on an observatory at 100 yards from the bank would be to alter the level by 0.1 second of arc. Hence the effect of an estuary or tidal river is likely to be much more marked than differential evaporation or rainfall. The author also considers the effects of the attraction of the sun and moon, producing as they must "tides" in the solid crust of the earth, on the reading of a level, and the measured altitude of a star as obtained with an artificial horizon. Finally, the author considers the light the measurements on the velocity of propagation of earthquake disturbances throw on the credibility of the hypothesis he has made as to the elastic constants of the earth. He shows that the two observed velocities of 2.5 and 12.5 kilometres per second would lead to values for Young's modulus and the rigidity below those found in the case of iron; the bulk modulus, however, obtained is very high, and this he considers quite probable, on account of the enormous pressure to which the earth's deep-seated material is subjected.

Prof. PERRY said he had thought of taking up the subject from an experimental point of view, and trying the effect of loading a large block of indiarubber. He had not had time to refer to the author's paper, in which the reasons were given for taking the earth as incompressible. He (Prof. Perry), however, thought that this assumption led to results in contradiction to actual observed facts. Prof. Milne had obtained results which, for want of any other explanation, he had been compelled to attribute to meteorological causes. The reason Dr. Chree had obtained so small a value for the effect of loading by surface water might be because he had assumed erroneous values for the elastic constants. If he took a value for Poisson's ratio such as we meet with in practice, the effects would

be much larger. Prof. Darwin had also investigated the folding of the surface of the earth due to loading. The results obtained by the author with reference to the velocity of waves did not seem quite satisfactory. The small waves which were found, both at Berlin and the Isle of Wight, to precede the main waves coming from an earthquake in Japan, were not accounted for. The wave velocity, in an infinite mass of steel (a very elastic material) was about 6 kilometres per second, which was very different from 12.5 kilometres per sec. The author had assumed such values for the elasticity as would give the correct velocity.

The author, in reply, said that in applying the equations of elasticity to the earth's interior, unless the material were supposed nearly incompressible, one obtained values of the strains too large to be consistent with the fundamental mathematical hypothesis that the squares of strains are negligible. In the case of surface loading no such restriction was necessary, so far as the surface layers at least are concerned. The differences between the several numerical estimates for the ratio of gravitational and pressure effects of a surface load were principally due to the differences in the hypothetical values ascribed to the rigidity. It was his wish to make it clear that the pressure and gravitational agencies treated in detail in the paper were not the only ones likely to affect the level; he had specially called attention to solar heating and possible direct influence of moisture on the foundations of buildings, &c. The reason why for the one wave-velocity so much higher a value was obtained than that Prof. Perry calculated for steel was solely the high value, 24:1, found for the ratio of Thomson and Tait's elastic constants m and n . He knew Prof. Darwin had treated of the phenomena met with in loose earth in some cases, but could not say whether this was what Prof. Perry referred to. He had himself once thought of attempting an application of what Prof. Karl Pearson termed the "equations of pulverulence," as treated in detail by Prof. Boussinesq, but had not done so, partly from a feeling of uncertainty as to their physical value. Supposing these equations satisfactory, they ought to give better results than the equations of elasticity when surface load was applied to a deep alluvial soil.

A paper on "*Musical Tubes*," by Mr. R. T. RUDD, was, in the absence of the author, read by the Secretary.

The author has examined a set of tubes ranging in length from 95 inches to 12 inches, made out of "1-inch" gas-tube. Having tuned these to a diatonic scale, he found that there was a very marked difference in the character of the sound of the long, the middle, and the short tubes. Commencing with the long tubes, the first two octaves have a full rich tone, very similar to that of a church bell. They range from D of 145 vibrations per sec. to D of 580 vibrations. At about this point the tone changes from that of a church bell to one peculiar to tubes; the note also falls back in the scale more than a fifth, viz., to F $\sharp$ (360), the same tube giving two notes, to either of which the attention can be directed. In order to distinguish these different classes of sound produced by tubes, the author calls the tone corresponding to that of a church bell the "low grade," the next one the "middle grade," and that produced by short tubes (27 inches and under) the "high grade." At the junction between the high and middle grade there is a fall in the notes of about an octave and a half. The following formula may be used for calculating the pitch of the note given by a tube:—

$$V = \frac{DC}{L^2};$$

where V = frequency, D = external diameter, L = length, and C is a constant, which for iron tubes has the values 100×10^4 , 62×10^4 , or 22×10^4 , according as the note belongs to the low, the middle, or the high grade.

The author explains the effects by a consideration of the partial tones present and their effect on the ear.

Prof. RÜCKER said he thought it a great pity that in England such confusion of nomenclature existed, so that partials were often called overtones. He considered that the author had made an extremely ingenious attempt to explain the differences of pitch observed; this explanation apparently resembling that given by Prof. Everett to account for combination tones. The author explains the presence of a note of frequency 630 as being formed in the ear by the harmonics having frequencies of 1260, 1900, and 2600. He also explains the absence of lower partials having frequencies of 780, 390, and 140, by the supposition that they are so far removed from the "focus" as not to appreciably affect the ear. Another explanation of the presence of a note of frequency about 630 would, however, be the formation of a difference-tone between the partials of frequency 780 and 140.

Mr. BLAILEY agreed with Prof. Rücker as to the vagueness of the terms often employed, and said that it appeared that in the "high grade" the note was caused by the first proper tone in the "middle grade" by the second, and in the "low grade" by a difference-tone produced by the fourth, fifth, and sixth proper tones. The distance of the nodes from the end of the tube was 0.224 of the length and not 0.25, as the author states, and in the case of a tube clamped at the node this difference in the position of the clamp would have a marked effect on the tone. A great difference in the tone was also produced by varying the hardness of the hammer.

Prof. AYRTON said he had once investigated the behaviour of some tubes by analysing the note given out by means of a Helmholtz analyser. In the case of the tubes that gave a good note it was found that the components were few and well marked; while in that of the tubes which gave a bad note, the components were numerous and sometimes very ill-defined. The relative length, diameter, and thickness of the tube had a great influence on the tone.

The Society then adjourned till January 22, 1897.

NOTICES OF BOOKS.

Cycling as a Cause of Heart-Disease. By GEORGE HERSHELL, M.D. (Lond.). London: Baillière, Tindall, & Cox. 1896. Pp. 46.

To the best of our non-professional judgment the author makes out his case very well. But is he, perhaps, not going too far to assert that a popular fad is almost certain to be physically or morally injurious?

Scientific Exploration in Balloons.—M. Mascart. —A number of captive balloons were sent up from different stations in the night between November 13th and 14th, and at the same time free balloons ascended from other stations. The free balloon sent off from Paris rose to the height of 15,000 metres, and recorded a temperature of -60° .—*Comptes Rendus*.

Determination of Nitric Acid in the Waters of the Seine, the Yonne, and the Marne, during the last Floods.—Th. Schloesing.—The proportions of nitric acid carried down respectively by these three rivers in twenty-four hours were 351,000, 54,000, 107,000, and 486,000 kilos. It is remarked that the months of June, July, and August have been exceptionally rainy.—*Comptes Rendus*.

CORRESPONDENCE.

THE PROXIMATE CONSTITUENTS OF COAL.

To the Editor of the Chemical News.

SIR,—May I be permitted to add my protest to that of Messrs. Cross and Bevan (CHEMICAL NEWS, lxxiv., p. 294).

Not only is my note "On the Action of Dilute Nitric Acid on Coal" condensed into about twenty words,—of which perhaps I have no right to complain,—but it is preceded by an abstract ten times as long, taken from the note book of Mr. S. Shaw, a colleague of the Secretary to the Committee.

Of course I am the last person to protest against the superior value assigned to a research when made by a College lecturer, even when that value is 10 : 1, and it has not been published; but I do object to my results being misrepresented.

I am made to say that "a considerable portion of the coal is converted into a black insoluble acid."

Now my note contains the following:—

"The insoluble matter from 90 grms. of coal was found to be 12.5 grms. consisting of coarse particles of coal-sand, &c.

"One gm. of coal, ground in an agate mortar and similarly treated, left only a trace of insoluble matter, so that in some varieties of coal the whole of the organic matter of the coal undergoes change." (*Proc. Chem. Soc.*, viii., 10, Feb. 1, 1892).

After this one is not surprised to find that Mr. Shaw's method, which it is suggested by the space, position, and date assigned to it, anticipated mine, consisted in treatment for three weeks with nitro-sulphuric acid, and that a "considerable proportion" thus became soluble in caustic alkali, whilst my process consisted in treatment with 49 per cent nitric acid, for six hours, the temperature being gradually raised toward the end of the time to 100° , and that thus the whole of the coal became soluble in dilute carbonated alkali.

I have since pushed these researches much further, on a large scale and on many coals, and hope some day to publish more complete results.—I am, &c.

R. J. FRISWELL.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 21, November 23, 1896.

Michel Lévy was elected a member of the Mineralogical Section of the Academy of Sciences *vice* the late M. Daubrée.

Various Properties of the Uranic Rays.—Henri Becquerel.—This paper will be inserted in full.

Discharges of the Röntgen Rays; Influence of Pressure and Temperature.—Jean Perrin.—At a constant temperature, and for one and the same gas, the quantity of electricity dissociated per unit of mass is independent of the pressure and proportional to the absolute temperature.

Illusions which accompany the Formation of Penumbrae. Applications to the X Rays.—G. Sagnac.—This paper requires the three accompanying figures.

Action of certain Hydrogen Compounds upon Thionyl Chloride.—A. Besson.—Not suitable for abstraction.

Crystalline Neutral Magnesium Chromite.—Em. Dufau.—At the elevated temperatures produced by the electric arc chromium sesquioxide combines directly with magnesia, without any intermediate agent, yielding neutral chromite, $\text{Cr}_2\text{O}_3\cdot\text{Mg}$, in octahedral crystals. Whatever the intensity of the arc employed we obtain nothing comparable to the calcium or the barium compounds, $\text{Cr}_2\text{O}_3\cdot 4\text{CaO}$, or $4\text{Cr}_2\text{O}_3\cdot\text{BaO}$, the neutral compound being always obtained.

Salts of Hexamethyleneamine.—M. Delépine.—A thermo-chemical paper. Hexamethyleneamine is a very feeble base.

Rôle of Boric Acid in Glasses and Enamels.—L. Grenet.—An excess of base occasions denitrification; that is, the crystallisation of definite borates and silicates. An excess of boric acid separates the glass in the bath into two layers, the upper being boric acid almost pure, and the lower glass saturated with boric acid.

Detection of Caramel in Wines. Possible Confusion with the Coal-tar Colours.—A. J. de Cruz Magalhães.—This paper will be inserted in full.

Zeitschrift für Analytische Chemie.
Vol. xxxv., Parts 4 and 5.

Determination of Saccharin in presence of Salicylic Acid.—Haers proposes (*Wochenschrift f. Brauerei*) to eliminate the latter by conversion into sparingly soluble dibromsalicylic acid.

Examination of Tanning Materials.—Notices of a number of papers by Jocum (*Leather Manufacturer*), Weiss (*Der Gerber*), Cezch (*Der Gerber*), Schröder and Bartel (*Dingler's Polytech. Journ.*), H. Krug (*Journ. Am. Chem. Soc.*).

Determination of Starch in Cereals, Potatoes, and Commercial Starches.—A series of papers by R. Sachsse and R. H. Chittenden (*Journ. of Analyt. Chem.*), Bauer (*Chemiker Zeitung*), H. Ost (*Chemiker Zeitung*), P. Guichard (*Journ. der Pharmacie*), Soxhlet (*Wochenschrift für Brauerei*), L. Sartagni (*Studi e ricerche del Lab. di Chimica agraria di Pisa*), Lintner and Dull (*Zeit. Angew. Chemie*), Munsche (*Chemiker Zeitung*), Winton (*Journ. Anal. Chemistry*), Reinke (*Dingler's Polyt. Journal*), Schreib (*Zeit. Angew. Chemie*), Berger (*Chemiker Zeit.*), J. Krieger (*Chemiker Zeit.*), Asboth (*Repert. Anal. Chemie*), Lintner (*Zeit. Angew. Chemie*), Leclerc (*Journ. der Pharm. und Chemiker Zeitung*), &c.

Table of Corrections for the Klosterneuburg Must Glass.—Drawn up by H. Pfeiffer (*Weinlaube*).

Spanish Earth for Clarifying Wines.—J. Nessler.—(*Weinlaube*).

Detection of Dulcin in Beverages.—A. Jorissen (*Journal de Pharmacie de Liège*) uses a solution of mercury nitrate free from any excess of acid. Dulcin, insulated according to Morpurge's process, is suspended in 5 c.c. of water, and heated with 2 to 4 drops of the reagent in a boiling water-bath for five to ten minutes, when, if dulcin is present, the liquid takes a violet-blue colour.

Colour Reactions of Saffron and its Adulterants.—A. Tschirch and O. Oesterle.—A tabular conspectus.

Chicory in Belgium.—Only the root of wild chicory may be used in groceries.

Volumetric Determination of Iron in the Ash of Plants and Animals.—M. Ripper (*Chemiker Zeitung*).—An iodometric process.

Detection of Small Quantities of Hydrogen Peroxide in Organic Fluids.—A. Richardson.—From the *Journal of the Chemical Society*.

Determination of Alumina in the Ash of Plants.—M. Berthelot and G. André.—From the *Comptes Rendus*.

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THE PROGRESS OF SPECTROSCOPY.

By H. KAYSER.

As I here, for the first time, give a survey of the development of spectrum analysis, I may be permitted not merely to keep the past year in view, but to reach further in order to render the sequel more intelligible. Whilst the discoverers of spectral analysis—as the very name implies—thought of qualitative analysis, this application has scarcely held good; there are only a few elements for which chemists utilise the spectroscope in this direction. The enormous enthusiasm with which the discovery of Kirchhoff and Bunsen was received disappeared, therefore, with relative rapidity. The interest in spectroscopy was revived in 1867 by the discovery of the gaseous nature of the protuberances, the lines of which showed further displacements from their correct positions, and thus by the application of Doppler's principle, led to determinations of velocity. Lockyer especially worked energetically; he undertook a re-determination of the spectra of the elements, but failed in this enterprise, which led him to the hypothesis that all the elements were compounded of ingredients which are common to many of them.

Although spectroscopic work never came quite to a stand, there elapsed a decennium before a real new impulse can be signalled, which still continues and daily bears new important fruits. The main cause of this impulse may be sought in two circumstances: the construction of Rowland's gratings, especially the concave gratings, and the following applications of photography. Gratings existed since the beginning of the century, when they were introduced by Fraunhofer, but they were much too small, and therefore feebly illuminating, too inaccurately divided, and, finally, much too expensive to compete with prism apparatus. But, on the one hand, prisms were used, and on the other the visible part of the spectrum, which was best known by ocular inspection, could not be photographed until H. W. Vogel had rendered his principle of optical sensitiveness practically available by the invention of the plates sensible to colours (1884). The old spectrum analysis had been wrecked on the circumstance that the spectra of the several chemical elements could not be determined with sufficient accuracy and completeness. We had scarcely advanced so far as to determine in the visible part the wave-lengths of the main lines to an Angström unit (A. U. = 1 ten-millionth m.m.). But as often a dozen lines of different elements fall within an A. U., it was found impossible to ascertain the chemical constituents of a substance from its spectral lines. The first condition for a faithful development was, consequently, a more accurate determination of the spectra of the elements. This task was undertaken since 1878 by Liveing and Dewar, who, for the first time, obtained a true insight into the ultra violet spectra of some elements, whereby they evaporated the substance in the electric arc. Hartley and Adeney carried out similar measurements for the spark spectra. But excellent as were these determinations in comparison with those of an earlier date, they were insufficient, as they were not executed with Rowland's gratings; hence the dispersion did not suffice to attain the accuracy required. In most cases we may indicate a line as known when its wave-length is certain as far as 0.1 A. U., but after all this does not suffice, and for modern spectrum measurements we must consider 0.01 the limit of accuracy to be aimed at. This, however, can be attained only by such great dispersions as

Rowland's gratings admit of, and hence Rowland was the first to publish measurements in which the $\frac{1}{1000}$ of an A. U. was given. They referred to the solar spectrum, and appeared with the splendid atlas of the solar spectrum which Rowland obtained in a purely photographic manner, and published in 1889. A systematic measurement of the spectra of the elements, photographed by means of Rowland's concave grating, and in which an accuracy of at least some hundredths of an A. U. was attained, was undertaken in 1887 by Kayser and Runge. Hitherto only the arc spectra of the alkalis, the alkaline earths, of Fe, Cu, Au, Ag, Zn, Cd, Hg, Al, Ir, Ti, As, Pb, Bi, Sn, Sb, have appeared, but other elements are to follow. More accurate measurements of limited parts of some spectra have also been published by Hasselberg and Rowland.

With the aid of such measurements it will now be possible to effect trustworthy qualitative analyses; though it must be admitted that the need for such will rarely occur. Spectral analysis is mostly too delicate for general chemical uses; it shows everywhere traces of impurities which are chemically far from distinguishable and of no significance. But in many cases, e.g., in the determination of the atomic weights of the elements, the chemist ought to ascertain the purity of his substances spectroscopically.

A comparison of the solar spectrum with the spectra of the elements was effected by Rowland (1891), and led him to the result that there are present in the sun: Fe, Ni, Ti, Mn, Cr, Ca, C, Va, Mo, Pd, Mg, Na, Si, Zr, Ce, Ca, Sc, Nd, La, Y, Nb, Er, Zn, Cu, Be, Ge, Sr, Ba, Al, Cd, R, Sn, Pb, K. Not present are: Sb, As, Bi, B, Ni, Cs, Au, In, Hg, P, Rb, Se, S, Tl, Pr. The other elements are doubtful or not yet examined. In the last year Rowland has begun to publish a list of the wave-lengths of all the refrangible lines.

Probably the most important advance has been rendered possible by the more accurate measurement of the wave-lengths. As far back as thirty years ago, we had begun to search for relations between the wave-lengths of the lines of one and the same element, as also between the lines of different elements. As we assume the vibrations of the ether corresponding to the different lines are directly excited by the vibrations of the atoms, as, moreover, the vibrations of a body depend on its mass, and on the forces acting upon it, so that as soon as these are given all the vibrations which the body can execute are firmly determined. We must expect that all the lines of an element are in regular connection, and may be included under a mathematical equation exactly as the different possible vibratory numbers of a string, an organ pipe, a bell, &c., can or might be regenerated by a formula. As the constants of such a formula depend on the mass of the energies of the atoms, i.e., on the same magnitudes which determine the chemical nature; as, further, in bodies chemically akin these magnitudes will be similar, it was to be expected that relations will be found between the spectra of bodies chemically allied to each other, and that such bodies would appear to be—so to speak—built on the same plan. Balmer first observed that the lines of the simplest spectrum known—that of hydrogen—can be represented by the equation—

$$\lambda = A \frac{n^2}{n^2 - 4};$$

where we then insert for n the numbers from 3 to 15, and A is a constant, 3647. All the lines are thus combined in a series. Kayser and Runge succeeded in showing that in the spectra of several elements there exist such series, which may be represented by the equation—

$$\frac{1}{\lambda} = A + \frac{B}{n^2} + \frac{C}{n^4};$$

inserting for n the series of whole numbers from 3 upwards, and for A, B, C different values which vary from element to element. The spectra of the alkalis appeared

built alike; they consist of three series of pairs of lines. In one of the series, comprising the strongest lines of the spectrum, the two lines of each pair move closer together as we approach the shorter wave-lengths. This series is called the chief series, in the others are the accessory series; in the latter the difference of vibration, *i.e.*, the difference of the number of vibrations of both lines remaining identical for all the pairs. In each series the brightness of the lines declines regularly with the increasing *n*, *i.e.*, the more we approach the ultra-violet. The two accessory series terminate at the same point of the spectrum. In Cu and Ag the same accessory series of pairs have also been found. In the spectrum of Mg, Ca, Sr the two series have also been shown, but they here consist not of pairs, but of triplets, arranged so that the difference of vibrations of the first lines is about twice as great as that between the second and third line. The same holds good for the groups Zn, Cd, Hg. In the groups Al, In, Tl finally the two series of pairs occur.

So far as the investigations have been hitherto extended, we may, therefore, by analogy of the spectra, distinguish the following groups:—1. Li, Na, K, Rb, Cs; 2. Cu, Ag; 3. Mg, Ca, Sr; 4. Zn, Cd, Hg; 5. Al, In, Tl. In each group the difference of vibrations of the pairs or of the two triplets increases with the atomic weight of the elements, and it is about proportional to the square of the atomic weight. In each group, with the increasing atomic weight, the spectrum advances continually to long wave-lengths, as if the heavy atoms vibrate more slowly. From group to group there occurs a considerable displacement of the spectrum towards the ultra-violet. For instance, the accessory series for Li end at 3498 Å. U.; for Na at 4069; for K at 4545; for Rb at 4776; for Cs at 5065. On the other hand, this end is displaced from Li 3498 to Cu 3165, to Mg 2514, to Zn 2328, to Al 2070. Hence follows the unpleasant result that for further groups of elements which belong together we have to seek the series among still smaller wave-lengths which cannot yet be photographed. Rydberg has arrived independently at similar results to those of Kayser and Runge, but he has sometimes arrived at untrustworthy conclusions by the use of old measurements.

A foremost and highly interesting application of these researches must be mentioned among the literature of last year: the work of Runge and Paschen on the gas evolved from clèveite.

In 1868 Lockyer discovered in the extreme cooling of the solar surface the so-called chromosphere, a very bright yellow line which does not occur as a dark line among the Fraunhofer lines, and had not been recognised in any terrestrial element. It was called the line D₃, and the hypothetical element from which it was produced was known as helium.

In the present year Ramsay discovered that the gas escaping from clèveite on heating or on boiling with sulphuric acid did not consist of pure nitrogen, as had been previously assumed, but contained at the same time a gas which remains after removal of the nitrogen, and is chemically quite indifferent. This gas showed in Geissler tubes the line D₃ in extreme strength, along with a great number of other lines. The existence of an element which had been assumed for twenty-seven years, on the evidence of a spectroscopic observation, was thus demonstrated. But did the clèveite gas consist of helium alone or were we in presence of a mixture of several new elements? The latter view was indicated by the experiments of Lockyer, in which certain lines appeared of a variable intensity. Runge and Paschen measured the spectrum photographically with a Rowland's grating, and found that its lines could be arranged in six series, three of which consist of narrow double lines. Of these, two possess constant differences of vibration and terminate at the same place; the third, which contains the strongest lines, contains couples of a decreasing difference of vibration. The three series thus form conjointly a spectrum which exactly corresponds to the type of the alkalis; these are the two

by-series, and the main series. The three remaining series of the clèveite gas display simple lines; the two fainter run out at the same place, and are therefore two by-series; the third is the main series. Runge and Paschen thus draw from their experiments the certain conclusion that the clèveite gas consists of two elements, and two only, as all the lines found are included by the six series. The first element is helium, the second has not yet received a name. The different position of the series further permits us to infer that helium has a higher molecular weight than the anonymous gas. The lines of both elements have long ago been observed in the chromosphere and in many stars. In the chromosphere the helium lines are decidedly stronger than those of the other gas. In many stars this is reversed, so that we find here a differentiation of the two elements in nature. This very careful investigation of Runge and Paschen's shows most plainly the importance of the series.

The third element, also discovered in the last years, argon, which Rayleigh and Ramsay succeeded in demonstrating in 1894 as a constituent of the earth's atmosphere, is hitherto characterised alone by its spectrum. According to the strength of the discharge passed through Geissler tubes filled with argon, it glows with a red or a blue light, and thus displays two quite distinct spectra, which were first photographed and measured by Crookes. Both spectra are as yet very imperfectly known. According to my own investigations, not yet quite completed, both spectra have not a single line in common. Whether argon is a new element, or a mixture, or—as some suppose—only a modification of nitrogen, can be decided only after a more thorough measurement of its spectrum. Hitherto I incline to the view that we have to do here with only a single new element. In many mineral springs there rise up bubbles of gas, which were formerly considered as nitrogen. I first observed that the gas from the Wildbad springs, along with nitrogen, contains considerable quantities of argon and helium. The same result has since been ascertained in various other springs. I have also detected the presence of helium in atmospheric air, that at least of Bonn.

Of the other spectroscopic literature of the last years, an entire series of researches by Eder and Valenta require especial notice. Thus the spectrum of the spark of carbon has been examined in all possible conditions, the absorption by different kinds of glass, and other bodies optically important; the ultra-violet spectrum of the flame reactions and other phenomena have been investigated. In mercury the authors found a band spectrum hitherto unknown; interesting because mercury forms a so-called monatomic gas, whence the possibility of various spectra would seem to many improbable.

In its astronomical applications spectroscopy has to record decisive results, though I must here confine myself to brief indications. In the nebulae it was formerly believed that hydrogen and nitrogen had been recognised; but Keeler has shown by his classical measurements that nitrogen is not present. On the other hand, numerous nebular lines have been photographically registered, mostly of unknown origin. The spectra of many stars have been of late photographed with much greater accuracy than it was formerly possible. Still, the results are far from being sufficient to unfold the chemical composition of the stars. The principle of Doppler has met with important applications. It shows that if a luminous body approaches us or recedes from us with the rapidity *u*, the lines in its spectrum are displaced towards the blue or the red, so that, instead of the true wave-length λ , there appears another, λ_1 , where—

$$\lambda_1 = \lambda \left(1 + \frac{u}{v} \right);$$

where *v* indicates the rapidity of light. From an observed change of the wave-length, *e.g.*, of the hydrogen lines, we may therefore calculate the velocity of a star towards us or away from us "in the radius of vision."

Such measurements have been very much improved by the introduction of photography, and they have been latterly carried out by different observers. In the same manner Keeler has been able to show that the ring of Saturn is no solid body, but consists of a number of small discrete parts—meteors. As the ring rotates, one side approaches us, whilst the other side recedes from us; the rays coming from the former side appear displaced towards the blue, and those from the latter side towards the red. Keeler observed that on the inside of the ring the displacement is greater than that on the outside; whence it follows that the ring is no continuous solid body.—*Chemiker Zeitung*.

DETERMINATION OF ALUMINA IN PHOSPHATES.

By HENRI LASNE.

THE determination of alumina in phosphates presents not merely a scientific interest, but a great commercial and industrial importance. We know, in fact, that the presence of sesquioxides is very detrimental to the manufacture of superphosphate.

If iron can be easily determined by means of standard solutions, the separation of alumina is difficult, and the methods proposed for this purpose fail, either from an inadmissible inaccuracy or from the great difficulty of their execution.

Solution of the Phosphate.—I prefer to treat with hydrochloric acid, evaporating to dryness in presence of the insoluble matter. The fluorides are completely decomposed, and the silica is rendered insoluble; these two conditions are indispensable, as the silica and the silicofluorides would accompany the alumina in its reactions.

To facilitate the execution of the procedure described below, it is well to re-dissolve in the smallest possible quantity of hydrochloric acid,—say 1 to 5 c.c. per gm. of phosphate,—to dilute with 20 vols. of water, and to heat. After thirty minutes the solution is filtered, and the filtrate is ready for the determination of the alumina.

In all the methods hitherto proposed the two sesquioxides are precipitated together, either in the free state or as phosphates. The precipitate is weighed and re-dissolved, the iron being thus determined volumetrically and the alumina found by calculation. This method would certainly be legitimate if we were sure of obtaining all the alumina and of knowing the exact composition of the precipitate obtained.

The separation of the phosphoric acid involves long and troublesome operations if we wish to obtain complete accuracy. Molybdic acid especially can only be separated from the sesquioxides by means of sulphuretted hydrogen.

The methods in which the sesquioxides are weighed in the state of phosphates fail as regards the base, as we do not know the composition of the precipitate obtained, which is very variable, as the following study shows:—

Precipitation of the Alumina in the state of Phosphate.—Two points have to be examined, the solubility of the precipitate and its composition.

In an acetic liquor aluminium phosphate is soluble enough to involve considerable losses, and to cause this method of precipitation or separation to be rejected irrevocably. The solubility diminishes on boiling.

In a solution very scarcely ammoniacal in presence of ammonium chloride the solubility is null, and the precipitation is entire.

I call attention to a method of precipitation which has not yet been applied. Ebullition for half an hour with ammonium hyposulphite suffices for complete precipitation (in place of three hours for pure alumina). The precipitate is easy to filter and wash: it is granular, like that of alumina in the Chancel process. The solubility

is so light that the greatest care is required for its detection.

The composition of the precipitate varies with the method, the degree of acidity of the liquid, and the excess of phosphoric acid which it contains, and that progressively.

The quantity of phosphoric acid combined with one and the same quantity of alumina is minimal in a slightly ammoniacal solution in which the neutral phosphate is partly dissociated, even when the liquid contains fifteen times more phosphoric acid than is necessary. In an acetic liquid, on the contrary, and especially in ebullition, the composition of the neutral phosphate is exceeded, even in presence of a very slight excess of phosphoric acid.

If we examine more closely the precipitation of ammonium hyposulphite, we see that the proportion of phosphoric acid in the precipitate does not regularly follow the excess contained in the liquor in which it is formed. If, on setting out from a liquid containing the elements of a neutral aluminium phosphate, we add increasing doses of ammonium phosphate, the proportion of phosphoric acid in the precipitate, at first below that corresponding to neutral phosphate, goes on increasing very rapidly up to a proportion representing an excess of 0.5 gm. phosphoric acid per litre; between 0.6 gm. and 1 gm. it remains stationary, and corresponds exactly to the neutral phosphate; beyond this point it is increased anew.

We obtain, therefore, the neutral phosphate exactly if we effect the precipitation in a liquid containing per litre 0.8 gm. of phosphoric acid in the state of ammonium phosphate, and this condition presents an elasticity sufficient to be easily realised.

When the liquid contains alkalis the aluminium phosphate carries down a certain proportion of these substances, forming a kind of lake.

The precipitate must be ignited before the blast for fifteen minutes, to lose entirely its water of combination.

New Method for the Separation of Aluminium.—Soda dissolves alumina in presence of an excess of phosphoric acid; all the bases which usually accompany it—i.e., lime, magnesia, iron, manganese—are entirely precipitated either as phosphates or as sesquioxides. In order that the separation may be complete the phosphoric acid must be in excess, otherwise there is formed a calcium aluminate insoluble in soda. If this condition is maintained not a trace of alumina remains in the precipitate. To be certain of this some precautions must be taken during the washing, to avoid the soda from becoming carbonated.

When the solution of alumina is obtained, two successive precipitations are necessary, since the second only enables us to obtain a pure compound of known composition.

For instance, for 1.25 grms. of phosphate, in a solution free from silica and slightly acid, we dissolve, in a capsule of nickel, 5 grms. of caustic soda free from silica and alumina, and 1 gm. of sodium phosphate. Into this we pour the solution of phosphate, stirring and keeping it at 100° for one hour. We make up to 250 c.c., and to take account of the volume of the precipitate we add, as a correction, 0.5 c.c. of water. We take 200 c.c. of the filtrate, continuing the operation with 1 gm., and thus avoiding any inconvenience from carbonation during washing.

The first precipitation is effected by acidulating, adding ammonium chloride, and then ammonia in very slight excess. The gelatinous precipitate would be difficult to wash, but this is needless. It is sufficient to drain it; it is then easily re-dissolved in hydrochloric acid, diluted to $\frac{1}{2}$, and heated.

To the solution thus obtained we add 3.5 c.c. of a 10 per cent solution of pure ammonium phosphate, to neutralise with ammonia without going as far as the production of a permanent precipitate, diluting to about $\frac{1}{2}$ litre, and adding 1.5 grms. ammonium hyposulphite. It is

boiled for half an hour, keeping the volume constant, then adding 5 drops of ammonium acetate in a saturated solution, and continuing the ebullition for ten minutes. It is filtered, and washed completely with hot water. It is ignited before the blast for fifteen minutes. The weight of the precipitate multiplied by 0.418 gives the weight of the alumina. We then add 0.8 m.grm. to take account of the slight solubility detected.—*Comptes Rendus*, cxxi., p. 63.

AN ELECTROLYTIC METHOD FOR THE DETERMINATION OF MERCURY IN CINNABAR.*

By W. B. RISING and VICTOR LENHER.

WHEN a rapid solution of cinnabar is desired, heretofore, oxidation with aqua regia has seemed most convenient; the length of time required to expel the nitric acid used, and the likelihood of loss of mercury by distillation in hydrochloric acid, are serious hindrances to the use of this method. Hydrobromic acid dissolves very readily mercuric sulphide, as well as many other naturally occurring sulphides with the evolution of hydrogen sulphide and the formation of the bromide.

If this solution be nearly neutralised with caustic potash, pure potassium cyanide added in sufficient excess to dissolve the cyanide first precipitated (Smith, "Electro-Chemical Analysis," p. 58), and electrolysed with a weak current, the mercury will be readily deposited as metal on a platinum dish used as a negative electrode. The use of hydrobromic acid is to be recommended, as it gives such a ready method of decomposition, and can be used at low temperatures, when there will be no loss of mercury by distillation.

The hydrobromic acid used in the following experiments was prepared by treating potassium bromide with sulphuric acid of 56° Baumé; the gas was conducted into water, as in the preparation of hydrochloric acid. By using potassium bromide with the above strength of acid, hydrobromic acid quite free from bromine can be readily prepared.

The ordinary hydrobromic acid used in the laboratory, containing bromine, could be used in the following experiments:—

The first sample which was worked with was pure mercuric sulphide. Hydrobromic acid of constant boiling-point—i. e., 49 per cent—was diluted with water 1 to 4, and the sample treated with as little excess as possible over what would be necessary for its solution; the slight excess of acid was neutralised with potassium hydroxide, potassium cyanide added in excess, and the solution electrolysed by a current giving 0.025 ampères N. D.¹⁰⁰.

The following results were obtained:—

Mercuric sulphide. Grm.	Mercury found. Grm.	Mercury per cent.
0.2110	0.1818	86.16
0.2058	0.1774	86.20

The second sample was a naturally occurring cinnabar; determination *a* was made, using the decomposition by aqua regia, evaporating off the excess of nitric acid with hydrochloric, neutralising the excess of hydrochloric acid with potassium hydroxide, adding potassium cyanide in excess, and electrolysed as before: *b* and *c* were treated with 20 per cent hydrobromic acid at the boiling temperature; solution was effected in a few minutes, the excess of acid was neutralised by potassium hydroxide, potassium cyanide added in excess, and electrolysed with the same strength of current as before.

Results were:—

	Cinnabar. Grm.	Mercury found. Grm.	Mercury per cent.
<i>a</i>	0.2024	0.1046	51.68
<i>b</i>	0.2514	0.1299	51.67
<i>c</i>	0.5135	0.2656	51.72

The last sample was a lower grade cinnabar, very silicious, and long digestion with either hydrobromic acid or aqua regia was necessary. In this last experiment the action of the hydrobromic acid was very much more rapid than that with aqua regia. The mercury was deposited from a cyanide solution as before.

Results were, using hydrobromic acid as solvent:—

	Cinnabar. Grm.	Mercury found. Grm.
<i>a</i>	0.2011	0.0616
<i>b</i>	0.2011	0.0622

Using aqua regia as solvent:—

	Grm.	Grm.
<i>a</i>	0.2030	0.0629
<i>b</i>	0.2030	0.0631

THE OXIDATION OF SILVER.

By CHARLES E. WAIT.

IN a former paper (*Trans. Am. Inst. Min. Eng.*, xv.) I had occasion to call attention to the large amount of silver present in a sample of bismuth litharge from a western smelting and refining company. The silver in this instance, estimated in the metallic state, was 2.94 per cent.

There was some doubt expressed as to the condition in which the silver existed, it being usually reported in the metallic state. Upon investigation it was found, as was shown in the paper referred to, that the silver did not exist wholly in the metallic state, but partly in another form, probably the oxide.

The conclusions reached at that time were based upon the following experiments:—

1. A weighed sample of the litharge was boiled in acetic acid for about half an hour, the solution was filtered, and the filtrate gave no reaction for silver.

2. Same as above, but with continued boiling; the filtrate gave no reaction for silver.

3. A sample was placed in cold acetic acid, kept there for half an hour, then heated to boiling; the solution was filtered, the lead was precipitated, and in the filtrate silver was found to exist, corresponding to 19.25 per cent of the silver in the litharge. Other determinations gave closely agreeing results, and it is interesting to note that the residues contained grains of metallic lead or argentiferous lead.

I have placed the following interpretations upon the above results:—

In Nos. 1 and 2 if any silver in any form was dissolved in the acetic acid, it was in turn re-precipitated by boiling in the presence of metallic lead.

In No. 3 the silver dissolved did not in all probability exist in the metallic state; and in this case was not precipitated by the lead, or argentiferous lead, the solution being brought merely to the boiling temperature.

I have been led to the above interpretations by showing that neither metallic silver reduced to fine subdivision by mechanical means, nor silver freshly prepared by zinc from silver chloride, is soluble in acetic acid, while argentic oxide is soluble in that acid; and a solution of silver oxide in acetic acid was precipitated completely by metallic lead upon boiling.

If the oxides are decomposed at a temperature of 300° C. (Roscoe and Schorlemmer, vol. ii., Part 1), or less (*Journ. Chem. Soc.*, lxx., 316), how may we account for

* Contribution from the Chemical Laboratory of the University of California. From the *American Journal of Science*, xviii., p. 96.

the existence of this substance in a product so highly heated as the litharge from the refining furnace?

Berthier (Crookes and Röhrig, "Metallurgy") has observed that lead may be oxidised by oxide of copper, when melted together, and further consideration of the subject shows that certain metals may be oxidised by being melted with an oxide of another metal, this oxidation depending in all probability upon the excess of the oxide present. Silver does not appear to be oxidised by oxide of copper if the results in experiment No. 18 are trustworthy.

According to Fournet's experiments (*Erdman's Journal*), silver is not an exception to the metals to which litharge gives up a part of its oxygen when fused with them for a considerable time.

While it is true that in the process of cupellation there is a loss of silver due possibly to oxidation, yet I do not find any losses even in the most exaggerated cases at all comparable with the percentages of silver oxide which I have been able to produce by a simple, yet possibly new, method.

It seemed to me an interesting problem to ascertain, if possible, the conditions under which silver may be oxidised at a high temperature, and the conditions under which the oxide of silver, if thus formed, would remain as such.

Some interesting work has been done along a similar line (*Fourn. Chem. Soc.*, April, 1894); that is, a study of those oxides which are stable at high temperature, and those which are decomposed, but under neither head does silver seem to have been discussed.

So few observations have been made along this exact line, as far as I have seen, that I have been induced to make some investigations with a view to throw light upon the subject, if possible.

The general method of conducting the experiments, I will briefly state as follows:—Metallic silver in minute subdivision was incorporated with one of the several bodies mentioned below; this mixture was put in a cupel of bone-ash, or in a scorifier, and then placed in the muffle of an assay furnace and subjected to an oxidising heat.

After this operation the mass was removed to a mortar, pulverised, then digested with acetic acid to boiling, the solution was filtered; in case a lead compound had been used, the lead was removed by sulphuric acid, hydrochloric acid was then added. The silver chloride thus formed was filtered, dried, and wrapped in least pure lead foil, and then carefully cupelled.

There was thus obtained the silver, which was converted to argentic oxide—at least I assume it to be such—and it is interesting to note that the amount of silver converted to oxide, and tabulated below, shows a very great range—in fact, from only a trace to as much as 39 per cent of the silver used.

This variation seems dependent upon a number of conditions, namely, the body with which the silver was mixed, duration and condition of heat, whether low, medium, or high temperature. As I did not use a pyrometer to ascertain the temperature during these experiments, I have thought it desirable to indicate the degree of heat approximately by such terms as "low," "medium," and "high," referring to the condition of the heat as usually obtained in the muffle in the assay of silver.

I append herewith several tables of experiments and results:—

TABLE A.

No. of expt.	Ag in grms.	Heated with—Grms.	Time of heat. Minutes.	Condition of heat.	Ag as Ag ₂ O. Per cent.
1.	0.5	2.5 MnO ₂	60	Medium	9.40
2.	0.5	5.0 MnO ₂	60	"	7.78
3.	0.5	2.5 Fe ₂ O ₃	60	"	None
4.	0.5	2.5 Bi ₂ O ₃	60	"	"
5.	0.5	2.5 ZnO	60	"	"
6.	0.5	2.5 CaCO ₃	60	"	"

From the above it will be seen that silver oxide was produced, and remained as such where manganese dioxide was used, and in no other case; it would also seem that this oxide was made at the expense of the manganese dioxide, and not by atmospheric oxidation, nor does it seem to have been produced in Experiment 3 (certainly not remaining as such), assuming the possible conversion of Fe₂O₃ to Fe₃O₄ (*Fourn. Chem. Soc.*, lxx., 313).

TABLE B.

No. of expt.	Ag in grm.	Heated with—Grms.	Time of heat. Minutes.	Condition of heat.	Ag as Ag ₂ O. Per cent.
7.	0.5	7.5 MnO ₂	30	Medium	34.16
8.	0.5	10.0 MnO ₂	30	"	18.84
9.	0.5	3.0 CaCO ₃	60	"	None
10.	0.5	3.0 Fe	60	"	"

The above results show that silver oxide was produced in the presence of manganese dioxide only; that less duration of heat than in Table A gives the amazingly large per cent of that oxide, and it furthermore seems that the oxide produced is not in proportion to the manganese dioxide used, but the reverse condition is generally seen in each set of experiments.

TABLE C.

No. of expt.	Ag in grm.	Heated with—Grms.	Time of heat. Minutes.	Condition of heat.	Ag as Ag ₂ O. Per cent.
11.	0.5	1 MnO ₂	2.5	High	32.24
12.	0.5	2 MnO ₂	2.5	"	34.28
12.	0.5	2 MnO ₂	20	"	11.72

The above experiments show, other conditions being the same, the longer the duration of the heat the less oxide there is produced.

TABLE D.

No. of expt.	Ag in grm.	Heated with—Grms.	Time of heat. Minutes.	Condition of heat.	Ag as Ag ₂ O. Per cent.
14.	0.5	5 PbO	10	Medium	38.85
15.	0.5	4 PbO ₂	10	"	35.12
16.	0.5	2 BaO ₂	5	"	12.28
17.	0.5	7 BaO ₂	10	High	2.04
18.	0.5	4 CuO	12	"	None

In Nos. 14 and 15 the mixtures were placed in scorifiers, and covered with 10 grms. of lead oxide.

In Nos. 16 and 17 the mixtures were placed in cupels and covered with 2 grms. of barium dioxide.

It is interesting here to notice that barium dioxide serves as an oxidising agent; that the amount of silver oxide produced decreases probably both with increase of time and temperature.

Although lead dioxide may readily give up a part of its oxygen, and thereby be converted into a lower oxide, yet the amount of silver oxide produced was no greater than with lead oxide alone; this is an interesting illustration of the property of lead oxide to serve as a possible carrier of atmospheric oxygen, producing silver oxide in a manner similar to that of the two bodies, manganese dioxide and barium dioxide, liberating oxygen. In the case of lead oxide, No. 14, if dissociation is not possible (*Fourn. Chem. Soc.*, lxx., 316) even at so high a temperature as 1750° C., it seems most reasonable to account for its peculiar oxidising action, as mentioned above, viz., as a carrier of atmospheric oxygen. Although copper oxide has been shown to yield up a part of its oxygen at 1500° C., yet I find no evidence of silver oxide existing in Experiment 18 in the remaining ignited mass.

TABLE E.

No. of expt.	Ag ₂ O in grm.	Heated with—Grms.	Time of heat. Minutes.	Condition of heat.	Ag as Ag ₂ O. Per cent.
19.	0.5	5 MnO ₂	60	Medium	36.4
20.	0.5	3 Fe	60	"	0.3
21.	0.5	3 CaCO ₃	30	"	0.2

In Table E a variation was made in the nature of the experiment. Freshly prepared silver oxide was used; while this oxide was completely decomposed upon being heated gently upon a porcelain lid; yet in No. 19, where manganese dioxide was used, it will be seen that 36.4 per cent of this silver oxide completely escaped decomposition.

The above results, in connection with others along a similar line, have induced me to believe that attention has not heretofore been directed to the ease with which silver may be oxidised by lead oxide, and particularly by substances which give up a part of their oxygen upon gentle ignition, such as manganese dioxide and barium dioxide. Is it not, then, reasonable to assume that certain losses, or irregularities in the treatment of silver and its compounds, may be due to this cause?—*Journal of the American Chemical Society*, xviii., No. 3.

AN IDEAL CHEMICAL LABORATORY.*

By Professor W. RAMSAY, F.R.S.

THE honour which has been done me in asking me to address you at the opening of these splendid new laboratories affords me an opportunity of making some remarks of a general nature on the use of a laboratory both to teachers and students. I entertain some very positive opinions on some matters connected with laboratories, partly based on innate conviction, partly on experience; and opinions, like clothes, require an airing occasionally, if only to preserve them from becoming moth-eaten, and to show where patches are required.

To begin, then, I hold that a laboratory should not be too large. You will in these days of exact Science, when mathematics invades even the microscope of the zoologist, request me to place an exact numerical value on the word "too." I will gladly do so. Too large means capable of containing more than forty or fifty students. But why not? Because students are, after all, human beings, and I do not believe that it is possible for any man to be interested in more than forty or fifty human beings all engaged in similar work. In the first place, it is difficult to remember the names of fifty people, and still more difficult to gauge their mental characteristics and be lenient to their mental aberrations. For this reason I prefer the number 40 to the number 50. One feels more at home with 40 than with 50 people. I should be still more pleased with 30, if they all were of sufficiently good calibre.

Of course it is as easy to lecture to five hundred as to fifty. And if, as in the old days, it were deemed sufficient for any one, designing in later years to be a barrister, a ship-builder, or an architect, that he should attend only lectures on chemistry, and not attempt laboratory work, and if it were the custom as in old days, not in order to prepare for any examination, but to acquire some knowledge of a subject, then we might be happy with lecture classes of any number capable of being reached by the human voice, and with laboratories filled with the *élite* of those classes; but now, when practical manipulation is required of every one who attends lectures, our lectures and our laboratories must, I suppose, be attended by the same—or by nearly the same—number of people. Hence if the laboratory is designed to hold forty, and only forty people, it is probable that our lectures, at least the general course, will be attended by the same number.

But what about assistants? Can they not, and do they not, bear the heat and burden of the day, contenting themselves with the skim-milk, and leaving the cream to the professor? To be sure they do; but that does not touch the fringe of the matter. For I hold it to be the

professor's duty (and his privilege) to know reasonably well each one of his flock: to borrow a simile—the food must be prepared by the cooks (I do not use this word in the technical sense which it bears in chemistry), and the physician must see that it is being digested, and when necessary administer aperient pills. In plain language, the professor must know what each man is doing, and whether he is doing it well.

Among the forty or fifty, supposing them to be equally divided over a three years' course, there will be ten or twelve who are reasonably well acquainted with analytical operations, who have made a sufficient number of preparations, and have acquired manipulative skill. Such men are anxious to advance the bounds of Science. Having for more than two years watched the fabric of chemistry growing under the architectural operations of the professor and his assistants, and of others, their seniors in academic life, who have entered the temple of research, they yearn and burn to follow such enticing examples. But they are as yet not sufficiently fertile in ideas. Sometimes, of course, a young and inexperienced student conceives great thoughts; but such persons are rare. It is necessary, therefore, that the impulse be given from without; that some bricks be added to the temple of knowledge, to fill up gaps left by the carelessness or too great hurry of former builders; or that long neglected dust-heaps be swept out in the hope of discovering hidden treasure. It is the duty and privilege of the professor to call attention to these *lacunæ* and *thesauri*, and to suggest means whereby the former may be bridged and the latter recovered. Now it is not easy for any one man to supply mental material to more than a very limited number of researchers or to keep clearly in his mind the details of many pieces of work. It is like playing ten games of chess blindfold, only considerably more difficult. True, the player can see the board, by cross-questioning the players as to their movements; but the power of independent motion of the pieces, and the unforeseen nature of the combinations, complicates the nature of the problems. Moreover, it is a game where the pieces are being continually shifted by outsiders who publish their moves, and it is necessary to pay attention to such changes. In short, it is difficult enough to carry out one research at a time; it is supremely difficult to superintend a dozen. Hence another reason for the limitation of numbers.

But there is still another. In a comparatively small laboratory an atmosphere of interest exists. The workers speak to each other in friendly intercourse, and criticise each other's work. The influence of seniors on juniors is felt. But in a large laboratory, where the principles of the factory supersede the kindly intercourse of friends,—where one is lost in labyrinths of passages, and puzzled by multiplicity of rooms,—where no one knows what his neighbour is doing, nor cares, such advantages are lost. For my part I prefer the gossip of a village to the County Council formalities of a city.

Lastly, in a larger laboratory, there is need of organisation. The chief, that is the professor, is busied in administration. Apparatus to be ordered; servants to be superintended and paid; students to be enrolled and registered; correspondence to be conducted—all this takes time, and takes time from one whose time should be otherwise spent. And these are duties which cannot be delegated; to be well done, they must be done by the chief; and the chief should be engaged in the duties I have specified before. These are pleas for not too large laboratories.

I will now advance a plea for a not too luxurious laboratory. I do not advocate a reversion to the kitchen of Berzelius, or to the still more compact tray of bottles, pipetstems, and candles of Wollaston, but I maintain that Heaven helps those who help themselves. To begin in the lap of luxury leads to effeminacy and incapacity. I can imagine a latter-day student, plunged in the penury of a works laboratory, weeping because no sulphuretted hydrogen is laid on; because to obtain steam he has to

* An Address delivered at the opening of the Gossage Laboratory of University College, Liverpool.

boil water; because a vacuum cannot be obtained without manual labour. As an engineer should be able to make his own tools, so should a chemist; starting with glass tubes he should be able to extemporise a blowpipe, and make the most complicated apparatus. He should be a reasonably good gas-fitter and turner; he should be able to solder a joint; and he should be able to turn to account almost every apparently useless article. Faraday's chemical manipulation is a storehouse of hints, but we have added to his store. Now if the student has a shop at the corner, where all possible things may be procured; if he works in a laboratory where he has merely to turn a stopcock and results pour out, he loses by not having passed through the ordeal of hard experience. A little time is lost; but here loss of time means gain in almost every other respect.

One word about the teaching of students. The theme of chemical education has been recently discussed within these walls, but on totally different lines from those which I propose to follow. My thesis here is that students are as a rule much overtaught. I should not regard that laboratory as a chemical heaven where every student had an assistant at his elbow, keeping him in the straight path, and guarding him from error. And taking for granted that the object in training students in chemistry is to teach them to discover new truths, and to form theories concerning the relations between old truths, it is best to adopt the well known method of trial and failure. A student gains much more knowledge, much more experience, and much more confidence, if, instead of following a printed guide, he attempts, *proprie motu*, to devise a new method (even when its failure stares in his teacher's face) and tries it. Indeed, there is far too much spoon-feeding. The frequent elementary treatises which supply "a long-felt want," and which repeat the boiled-down truisms of chemistry, are much on a par with the widely advertised foods for infants. Let the student, as far as possible, be left to devise his own processes and his own instruments, adapting to his immediate use what he finds in the laboratory; for that is what he ultimately will have to do when he starts for himself. There are two reasons which argue in favour of this course; it is much more beneficial for the student, and it is much less arduous for the teacher. Of course, like everything else, this process may be carried too far, but let the help be given as help, and not as a set of methods and rules. The one method of teaching turns out competent investigators; the other, competent workmen. But it is investigators that we should manufacture in such laboratories as this.

One word more and I have done. What is it that gains a student a position in making a start in the world? Is it a high degree? Not unless he wish to start as a schoolmaster, and then a competent knowledge of, and an intense interest in, the games of football and cricket are held in as high esteem. It is the good word of his teacher. And why do his teachers thus recommend him? Because they have studied and valued his character during the years of intercourse. That is the examination through which we all have to pass; a practical examination which lasts a lifetime. Would it not be well to award our science degrees by what, after all, is the only criterion of merit in the world, the judgment of those of our fellows capable of forming an opinion?

Many of those I am now addressing will follow a career in technical chemistry. For such, a knowledge of methods is indispensable. Engineers should work hand in hand with chemists; for many chemical processes depend for their success on the smooth working of the plant by which they are realised on a large scale. What yields good results with a grm. often fails with a thousand kilograms, owing to difficulty of treatment, which means expense.

But I do not think that it is advisable for young chemists to carry out experiments *en gros*; for first, it is a very expensive amusement, and second, as far as

chemistry is concerned, little is learned. But here again the happy mean must be sought. It is useful occasionally to attempt to carry out operations in iron and stone-ware vessels on perhaps a kilogram of material, so as to learn the different methods of treating small and comparatively large quantities of material.

The donors of this magnificent laboratory are men who have spent their lives in putting chemical theory into practice. As you know, Mr. Gossage and Mr. Timmis have raised this building in memory of Mr. William Gossage, the father of the former, and a great inventor in his day; and Sir John Brunner, Mr. E. K. Muspratt, and Messrs. Lever Brothers have aided most generously in providing necessary rooms. These are names which stand in the forefront of our chemical industry, and the history of the alkali trade in future years will rank their achievements on a par with the landing of Julius Cæsar, or the reign of King Alfred. It is to Mr. William Gossage that most of the important features of the alkali trade are due; for example, the condensation of hydrochloric acid, instead of allowing it to escape to pollute the air; the smelting of pyrites residues for copper; the utilisation of caustic mother-liquors of soda-crystals for the manufacture of caustic soda, and the utilisation of sulphur waste. But it is not my function here to enter into chemical details; I mention Mr. Gossage's name, and those of the other donors of these laboratories, in order that I may point to them as chemical products of a very high order, and invite those of you who are to make use of their magnificent donation, to follow in their footsteps, proving yourselves able to advance science, and to benefit your fellow creatures.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, December 10th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 2nd to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined all were found to be clear, bright, and well filtered.

The rainfall at Oxford during November again shows a serious deficiency, after an excess of 3.14 inches for the two previous months. The average fall for November is 2.42 inches, while the actual fall was 0.79, showing a deficiency of 1.63 inches, bringing the total deficiency for eleven months of the year to 4.46 inches, or about 20 per cent.

The numbers of microbes in the waters is keeping satisfactorily low. The following table shows our results:—

	Colonies per c.c.
Thames water, unfiltered	2223
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	62
Ditto ditto lowest	4
Ditto ditto .. (12 samples) mean	21
New River water, unfiltered	1054
New River water, from the Company's clear water well	20
River Lea water, unfiltered	1178
River Lea water from the East London Com- pany's clear water well	6

These figures prove the excellence of the Companies' filtering and storage appliances.

Having had our procedure attacked, we may as well put on record that since commencing the bacterial examination of the London waters in 1886, we have *always* used incubators properly controlled by sensitive gas regulators, and in no instance has the internal temperature varied beyond the proper limits, namely, in the case of gelatine cultures, between 20° and 20.5° C. To our surprise, however, in Dr. Klein's recent report to the London County Council he expresses himself in the following words:—

"I have seen it stated in the publications of the London Water Companies' analysts that during November these gentlemen counted the colonies, after forty-eight hours, in the plates *exposed to the ordinary temperature of the laboratory*, and found their numbers varying between seven and seventy. I have no hesitation in saying that no bacteriologist would accept these figures as representing the actual number of bacteria present in the water; only a fraction of the colonies develop in a gelatine plate after forty-eight hours if the plate is kept at temperatures below 17° or 18° C."

Further on Dr. Klein says:—

"The small number of microbes stated to be present in the London waters by the Companies' analysts are only to be explained by the imperfect methods used, *keeping the plates at the temperature of the laboratory*, and counting the colonies already after forty-eight hours, when they have barely commenced to grow." (The italics are ours).

Now, it will scarcely be believed that the above-quoted assertions, which Dr. Klein has made for the purpose of throwing discredit on our bacteriological results, have no foundation in fact. In none of our reports have we ever made any such statement.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

THE SEPARATION OF THORIUM FROM THE OTHER RARE EARTHS BY MEANS OF POTASSIUM TRINITRIDE.*

By L. M. DENNIS.

SOME time ago the author and F. L. Kortright (*Ztschr. Anorg. Chem.*, vi., 35; *Am. Chem. Journ.*, xvi., 79) briefly described the action of a solution of potassium trinitride upon a neutral solution of the rare earths. It was found at that time that the flocculent precipitate which is produced was most probably thorium hydroxide, but our supply of potassium trinitride having been exhausted it was impossible to further investigate the reaction or ascertain the completeness of the separation. The immediate continuation of the work was prevented by unexpected difficulties which were encountered in the preparation of pure hydronitric acid on a large scale. These difficulties have since been removed, and it has been

possible to prepare an amount of the reagent sufficient for the investigation described below.

The solution of potassium trinitride which was used was prepared by carefully neutralising a dilute solution of hydronitric acid with a dilute solution of pure caustic potash and then adding hydronitric acid sufficient to give to the solution a distinctly acid reaction. The solution first employed contained about 3.2-10 grms. of potassium trinitride to the litre.

Before studying the separation of thorium from the other rare earths, the reaction between potassium trinitride and pure thorium chloride was first investigated. The thorium employed was from a sample of thorium oxalate, which had been very kindly presented to me by Dr. Theodor Schuchardt, of Goerlitz. It was found to be of a very high grade of purity, but to guard against the possible presence of other rare earths, the oxalate was converted to the oxide by ignition, treated with concentrated sulphuric acid, the anhydrous sulphate dissolved in distilled water at a temperature of 0°, and this solution was precipitated with pure oxalic acid. The precipitated thorium oxalate was thoroughly washed with hot water containing 1 per cent hydrochloric acid, and was then dropped into a hot concentrated solution of ammonium oxalate. It dissolved completely, and no precipitate formed when the solution was diluted and cooled. From this solution the thorium was again precipitated as oxalate by means of strong hydrochloric acid, and was then brought into solution as thorium sulphate in the manner described above. It was then precipitated by ammonium hydroxide, and the precipitate thoroughly washed with water. The thorium hydroxide was then dissolved in hydrochloric acid, ammonium hydroxide was added until a faint but permanent precipitate remained, and this was then removed by filtration. There was thus obtained a neutral solution of thorium chloride containing a very small amount of ammonium chloride.

The strength of this solution of thorium chloride was ascertained by precipitating portions of 10 c.c. each with ammonium hydroxide, filtering, washing, igniting, and weighing as ThO₂. Two determinations gave for thorium oxide in 10 c.c., 0.0591 gm. and 0.0595 gm. The mean of these results is equivalent to 0.00521 gm. thorium in 1 c.c.

Upon adding to this thorium solution a few c.c. of the solution of potassium trinitride, the precipitate which, in the previous work with Dr. Kortright, had formed at once, failed to appear; upon heating the solution to boiling, however, there was quickly formed a white flocculent precipitate, closely resembling in appearance aluminum hydroxide, but settling rapidly when the flame was removed. In the first determinations the solution was boiled for five minutes, but it was later found that boiling for one minute is sufficient. During the boiling the odour of hydronitric acid was distinctly noticeable. The precipitate was washed by decantation with hot water, transferred to the filter, ignited, and weighed as ThO₂. Twenty c.c. of thorium chloride, containing, according to the determination with ammonium hydroxide, 0.1186 gm. thorium dioxide, gave, by precipitation with potassium trinitride, 0.1183 gm. thorium dioxide, equivalent to 0.00520 gm. thorium in 1 c.c. instead of 0.00521 as obtained with ammonia.

It is apparent, therefore, that thorium can be quantitatively precipitated by potassium trinitride.

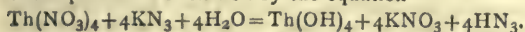
The previous work of Dr. Kortright showed that the thorium is probably precipitated as the hydroxide, but the tendency of the precipitate to absorb carbon dioxide rendered the analyses unsatisfactory. If, however, the thorium is precipitated as the hydroxide, then all of the hydronitric acid of the potassium salt first added must reappear in the filtrate from the thorium hydroxide and in the gas evolved during the boiling. To ascertain whether this took place the precipitation was made in a round bottomed flask. In the neck of the flask there was inserted a two-hole rubber stopper, through one

opening of which a current of purified air was admitted, the other opening carrying an upright condenser. The condenser was connected at the upper end with two absorption vessels containing neutral silver nitrate solution. As the hydronitric acid was to be determined by precipitation with silver nitrate, a neutral thorium nitrate solution, containing 0.0075 gm. thorium in 1 c.c., was substituted for the thorium chloride. The thorium nitrate solution was placed in the flask, potassium trinitride was added, and after starting a current of air through the apparatus, the contents of the flask was heated to boiling and kept boiling for two minutes. Soon after the heating began a white precipitate of silver hydronitride formed in the first absorption flask containing the silver nitrate; by the time the reaction was complete this precipitate had become quite voluminous. The absorption of the gas by silver nitrate seems to be both rapid and complete, for nothing more than a slight opalescence ever appeared in the second absorption flask. After the apparatus had become cool the thorium hydroxide was filtered off, and the filtrate was precipitated by silver nitrate. The silver trinitride thus obtained, together with that in the absorption flasks, was washed by decantation with cold water, the washings being passed through a hardened filter. When the wash water gave no further reaction for silver, the funnel with the filter was placed in the neck of the flask containing the main part of the precipitate, and quite dilute hot nitric acid was poured upon the paper. The silver trinitride on the paper dissolves almost immediately. After washing the paper with water, the funnel was removed, and the contents of the flask was boiled until all of the silver trinitride had dissolved. The silver was then precipitated by hydrochloric acid and weighed as silver chloride. Ten c.c. of thorium nitrate and ten c.c. of potassium trinitride were used. The silver chloride resulting weighed 0.1447 gm. equivalent to 0.0434 gm. hydronitric acid. The strength of the potassium hydronitride, which was a different solution from the one first employed, was then determined in the same manner.

5 c.c. gave 0.0744 AgCl = 0.02232 HN₃,

5 c.c. gave 0.0745 AgCl = 0.02235 HN₃.

Using the mean of these results, it appears that 0.0446 gm. of hydronitric acid was used in the precipitation of the thorium nitrate, of which 0.0434 gm. was recovered from the filtrate and distillate. That this latter result is somewhat low is doubtless due to the loss of hydronitric acid by volatilisation during the filtration of the liquid in the flask. These results, together with those given in the preceding article already referred to, enable us to represent the reaction by the equation—



This reaction is interesting not only because of the quantitative precipitation of thorium by this means, but also because of the peculiar behaviour of the potassium hydronitride. As Ostwald has stated, hydronitric acid is but slightly stronger than glacial acetic acid, and the above equation reminds one of the behaviour of acetates towards ferric iron, the solution of ferric acetate being fairly stable in the cold, but breaking down upon heating into acetic acid and ferric hydroxide.

The experiments detailed below were then made to ascertain whether thorium could be quantitatively separated from the other rare earths by means of the above reaction. A neutral solution of pure lanthanum chloride was first prepared, and its strength determined by precipitating with ammonium hydroxide and weighing the lanthanum as La₂O₃. The solution contained 0.00431 gm. lanthanum in 1 c.c. This solution gave no precipitate when boiled for some minutes with potassium trinitride. 15 c.c. of this solution and 15 c.c. of the thorium chloride solution were placed in an Erlenmeyer flask, 25 c.c. of potassium trinitride (3½ grms. to the litre) were added, and the solution was boiled for one minute. The precipitate was filtered off and washed with hot water, ignited, and weighed. To the filtrate 5 c.c. more of potassium

trinitride was added, and the solution boiled for two minutes. No further precipitation resulted. The solution was then precipitated with ammonia, and the lanthanum weighed as the oxide. The results were:—

	Taken.	Found.
Thorium	0.0781	0.0777
Lanthanum . . .	0.0646	0.0642

A mixture of the rare earths in Brazilian monazite was then freed from thorium by repeatedly digesting the mixed oxalates with a hot concentrated solution of ammonium oxalate. The residual oxalates were then transformed into chlorides and dissolved in water. The solution showed the pink colour and absorption bands of didymium, and gave a strong reaction for cerium when treated with hydrogen peroxide and ammonia. When boiled with potassium trinitride it gave a very faint precipitate, which was filtered off. By precipitation with ammonia, this solution of cerium, lanthanum, didymium, &c., free from thorium, was found to contain 0.0166 gm. of the mixed oxides in 1 c.c. The precipitation was made as in the separation from lanthanum, and an excess of potassium trinitride was used in each case.

	Taken.	Found.
I. Thorium	0.1300	0.1294
Ce, La, Di oxides	0.0332	—
II. Thorium	0.0785	0.0783
Ce, La, Di oxides	0.0830	—
III. Thorium	0.0535	0.0526
Ce, La, Di oxides	0.2490	—
IV. Thorium	0.0535	0.0531
Ce, La, Di oxides	0.2490	—
V. Thorium	0.0550	0.0541
Ce, La, Di oxides	0.4980	—
VI. Thorium	0.0555	0.0550
Ce, La, Di oxides	0.5810	—
VII. Thorium	0.0570	0.0558
Ce, La, Di oxides	0.8300	—

The recovery of the thorium is in all cases fairly exact, and the variation in the relative amounts of thorium and the other earths does not influence the sharpness of the separation. That thorium alone is precipitated by potassium trinitride is to be explained by its weak basicity. It is the weakest base in the whole group of the rare earths, with the possible exception of cerium in the ceric condition, and this higher form of cerium is probably incapable of existence in the presence of hydronitric acid.

We have, then, in potassium trinitride a reagent which can be used both for the qualitative detection of thorium and for its quantitative determination either alone or in the presence of other rare earths. So far as the author is aware, this is the only method as yet devised by which one of these earths can be quickly and accurately separated from the others, and that in a single simple operation.—*Journal of the American Chemical Society*, xviii., No. 11.

Society of Arts.—At the meetings of the Society of Arts after Christmas the following papers will be read:—"The Roller Boat of M. Bazin," by Emile Gautier; "Voice Production," by William Nicholl; "Irish Industries," by the Hon. Horace Plunkett; "English Orchards," by George Gordon; "The Prevention of Fires due to Leakage of Electricity," by Frederick Bathurst; "Dairy Produce and Milk Supply," by M. J. R. Dunstan, M.A.; "The Transmission of Power by Alternating Electric Currents," by W. B. Esson, M.Inst.C.E.; "London Water Supply," by Percy F. Frankland, Ph.D., F.R.S.; "The Chemistry of Tea," by David Crole; "The Evolution of the Silver Question," by Moreton Frewen, B.A.; "Children's Sight," by R. Brudenell Carter, F.R.C.S.; "Light Railways," by Everard C. Calthrop; "Cycling—Historical and Practical," by George Lacy Hillier.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 3rd, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 393).

164. "The Oxidation of Ferrous Sulphate by Sea-water, and on the Detection of Gold in Sea-water." By E. SONSTADT.

The experiments now described were made in the autumn of 1895, on sea-water supplied by the Great Eastern Railway Company in oak kegs, freshly filled, the water being stored in glass bottles as soon as received, and filtered before use.

I. On the Oxidation of Ferrous Sulphate by Sea-water.—In 1872 (CHEMICAL NEWS, xxv., 196, 231, and 241) the author gave a description of experiments proving the existence in sea-water of calcium iodate, four parts of this salt being shown to be present in one million parts of sea-water. As these experiments have not, within my knowledge, been repeated, and as I do not know of any analysis of sea-water recognising the presence of any salt therein capable of acting as an oxidiser, it seemed desirable to make direct experiment on the oxidising power of sea-water. To do this satisfactorily, it seemed necessary to compare sea-water against sea-water so treated as to reduce any salts of the nature of iodates that it might contain, due care being taken to thoroughly aerate the treated portion.

First Experiment.—1½ lbs. sea-water were evaporated to dryness with a small quantity (about 2 grms.) of pure mercury, and the residue was heated in a porcelain crucible into which a current of hydrogen was passed, until the mercury was completely expelled. The salts were digested in water, and the solution made up by washings to the original quantity. The solution was then put into a Winchester quart bottle, and repeatedly shaken up, the air being renewed from time to time. When it was judged that the aëration was complete, one pint of the solution was put into a bottle which it nearly filled, and 1 grm. of crystallised ferrous sulphate was added. A pint of the original sea-water was put into another similar bottle, with the same quantity of ferrous sulphate, and 1½ c.c. of dilute hydrochloric acid was added to each solution. The bottles were corked, and, after sufficient shaking to ensure mixture, were set side by side for three days, when the contents of both bottles were filtered simultaneously. After washing the precipitates with equal quantities of water, drying, and ignition, the ferric oxide from the natural sea-water weighed 0.0182 grm., and that from the treated sea-water 0.0132 grm.

Second Experiment.—This was conducted similarly to the first experiment, except that instead of evaporating the sea-water, with mercury, the latter was rubbed up with the residue left after drying, the subsequent heating in a current of hydrogen being conducted as before. Also, no acid was added to either the natural or the treated sea-water, and, after the addition of ferrous sulphate, the solutions were allowed to stand in the corked bottles for thirteen days before filtering. The natural sea-water gave ferric oxide 0.0540 grm. (after solution and re-precipitation 0.0528 grm.), and the treated sea-water 0.0270 grm. Thus the difference in this case, when no acid was added, and more time was allowed for the formation of the precipitates, was very much more than in the first experiment, and is greatly in excess of what can be due to the influence of the iodate present in the untreated sea-water.

Although in these experiments it was found impossible to completely dissolve the salts obtained after ignition, in the quantity of water required to form an equal volume with the original sea-water taken, yet there is no reason-

able ground for supposing that the change in composition thus effected could sensibly affect the oxidising power, apart from the reduction involved of the iodate, and other salts at present unrecognised, of a reducible character. The insoluble residue contained traces of several metals, all of which were not definitely recognised, an account of which I defer until an opportunity occurs to me of working upon larger quantities of material.

II. On the Detection of Gold in Sea-water by means of Mercury.—About 20 grms. of pure mercury was agitated in a flask with about half a gallon of sea-water for a long while, the flask being placed at intervals on a water-bath, so that the liquid became warm, though not hot. In subsequent experiments the water was not warmed, and no special proportion of mercury was used, though obviously the smaller the proportion of mercury the more agitation would be necessary to obtain the same result. The mercury was separated, washed, and dried with bibulous paper. The mercury was then volatilised in a porcelain crucible having an uninjured internal surface. A black adherent film remained, fixed at a red heat. When the crucible had cooled, a small quantity of strong hydrochloric acid was added, which, on warming, dissolved the greater part of the film, leaving, however, a stain not removable by repeated similar treatments. The acid solution being washed away, and the crucible dried, a drop or two of aqua regia was let fall on the stain, which was almost immediately dissolved. By cupellation a very minute gold bead was obtained. In some experiments the mercury that had been agitated with sea-water was distilled in a current of hydrogen, but on afterwards heating the black residue in the porcelain boat, in the open air, the residue was not adherent, and could not therefore be treated as described. To obtain an adherent film, 4 to 5 grms. of mercury must be left for volatilisation in the open. The mercury that is distilled off in a current of hydrogen is quite pure; but that volatilised in contact with air is not pure, for if a portion of it be condensed on a cool surface, and then volatilised, a residue remains which disappears on strong heating. Silver is one of the metals dissolved out from the black residue by the hydrochloric acid with which it is treated. This fact, although somewhat outside the subject of the present paper, is worth mentioning, as having a bearing upon the question as to the condition in which the precious metals are present in sea-water. Mercury does not decompose silver chloride, either in the wet or dry way, and yet it separates silver from sea-water. The most natural inference appears to be that the silver salt in sea-water is so far attenuated by dilution as to have undergone molecular disruption, so that it may be considered to be present as metallic silver in solution. If this be so in respect to silver, the gold in sea-water is probably also in a similar condition.

A comparison cannot be instituted between the simple and easy process now described, for detecting the presence of gold in sea-water, and the processes given in the author's paper "On the Presence of Gold in Sea-water" in 1872 (CHEM. NEWS, xxvi., 159), because the sea-water that comes in kegs from the sea-side is very much poorer in gold than the water of the Irish Sea, on which the author's earlier experiments were made. When some gallons of sea-water, furnished by the Great Eastern Railway Company, were heated with ferrous sulphate and a little hydrochloric acid, and the precipitate, after a few days, collected, the minute gold bead from this precipitate (which was lost by accident before it could be weighed) was certainly but a small fraction of what the same quantity of sea-water previously experimented upon would have yielded. Whether this poverty in gold of the sea-water is due to its brief contact with wood, or to the circumstance that it is taken from shallow water near the shore, where a certain admixture with mud or clay is inevitable, may be doubtful. But it is probable that finely divided clay, mixed with sea-water, would carry down with it, in settling, most of the gold present.

NOTICES OF BOOKS.

Select Methods in Inorganic Quantitative Analysis. By BYRON W. CHEEVER, A.M., M.D. (late acting Professor of Metallurgy in the University of Michigan). Third Edition, revised and enlarged, by FRANK CLEMENT SMITH, B.S., E.M., Professor of Geology, Mining, and Metallurgy, State School of Mines, Rapid City, S.D. Edinburgh: W. F. Clay, 18, Teviot Place. 8vo., pp. 154. 1896.

THIS able work, although published in Edinburgh, has evidently been written in America, and with a reference to American conditions. Thus we find tables for the use of Baumé's hydrometer, and mention of "casserole" as vessels in which to effect solution in acids.

The work does not include in its scope all classes of inorganic substances. The substances omitted are of little practical or commercial moment, but their unexpected occurrence may complicate the procedure required and lead the student astray. Among the poisonous metals which may possibly occur in the waste waters of industrial districts, are those especially where dyeing is carried on on a large scale.

By a printer's oversight, the capacity of the British gallon has been given as 7000 fluid grains. In all the substances touched upon the instructions given are not only accurate but full.

Treatise on Distillery: Industries of Distillation, Ferments, and Alcohols. ("Traité de Distillerie: Industrie de la Distillation, Levures, et Alcohols"). By M. P. GUICHARD, Member of the Chemical Society of Paris. Paris: J. B. Baillière et Fils. Pp. 388.

THIS work is one of the valuable series of scientific and technical treatises issued by the firm of J. B. Baillière and Sons. The subject is one which has attracted much thought and attention in France since the vineyards of that country have been ravaged by the phylloxera. We cannot help pointing out that when that scourge first invaded France, some of the leaders of the "Temperance" movement openly rejoiced in the delusion that the result would favour their cause. But, alas! the amount of alcoholism in France has not decreased since the destruction of so many vineyards.

Alcohol, of a sort, is manufactured from a variety of other substances. There are alcohols distilled from potatoes, from beet-root, from beet-root treacle, from Jerusalem artichokes, &c., &c.

The author expresses his gratitude for the fact that France is not exposed to the inroads of whisky. So be it, but we may in turn rejoice that we are as yet exempt from potato-whisky—the scourge of North Germany,—and from absinthe, the most deleterious of all spirituous liquors.

M. Guichard treats first of the manufacture of saccharine liquids, by the agency of malt and by acids, and on the fermentation of different classes of substances.

He then proceeds to the industry of ferments, an art in which France has been of late eminently successful. Next we come to the manufacture of alcohol and its purification.

On the use of alcohol as a drink the author takes a stand which we think will prove almost, if not entirely, satisfactory to the shade of the late Sir B. Richardson. He contends that alcohol is not a food, there being no true foods but substances which enter into the constitution of our body, and he gives tables showing the proportion of impurities contained in different ardent spirits. It would appear that the first and most costly Cognacs are often less pure than the "industrial alcohols." Among the more dangerous liquors he classes not only

absinthe and vermouth, but anisette and chartreuse! Pure alcohol he admits, however, is five times less dangerous than the essences which it contains.

A useful appendage is the vocabulary of the French, English, and German terms for the substances, the plant, and the operations occurring in the distiller's business.

Unfortunately the English equivalents for French and German terms are largely incorrect.

Exercises in Practical Chemistry, mostly Quantitative; being the Appendix to "Chemistry for Beginners." By R. L. TAYLOR, F.I.C., F.C.S. London: Sampson Low, Marston, and Co., Ltd.

THIS is one of that ever-numerous class of books in which we can find nothing to blame, and at the same time are at a loss to recognise a *raison d'être*. We can only hope that some day the beginners will reach maturity, and pour upon us a flood of results.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 22, November 30, 1896.

Scientific Exploration in Balloons.—M. Mascart.—Already inserted.

Determination of Nitric Acid in the Waters of the Seine, the Yonne, and the Marne, during the last Floods.—Th. Schloesing.—Already inserted.

Absorption of Nitric Oxide by Ferrous Bromide.—V. Thomas.—Ferrous bromide in an aqueous solution absorbs nitric oxide according to the law of Gay-Lussac. In a future paper I shall show that the ethereal solution behaves quite differently, and that by suitable arrangements we may obtain a solid compound perfectly crystalline like the chloride.

Tempering Steel with Phenic Acid.—M. Lowat.—Steel tempered in phenic acid acquires hardness, elasticity, and suppleness.

Action of Permanganate on the Polyatomic Alcohols and their Derivatives.—L. Perdrix.—In general the products of the oxidation are formic acid and carbonic anhydride. To this rule the monatomic alcohols form exception.

Zeitschrift für Analytische Chemie.
Vol. xxxv., Parts 4 and 5.

Detection and Determination of Sulphocyanogen in Technical Ammonium Sulphate.—Offermann.—This process cannot be effected by means of ferric chloride in an aqueous solution. The solid salt must be extracted with alcohol. For the quantitative operation, 5 grms. of the salt are extracted for an hour with absolute alcohol, and the sulphocyanogen may be determined colorimetrically by comparison with a specimen of known strength.—*Apotheker Zeitung*.

Determination of the Colouring Power of Litmus.—E. Dieterich (*Helfenberg Annalen*).—Already inserted.

Determination of Insoluble Residue in Isinglass.—E. Dieterich.—Ten grms. of the material are cut into fine slips and boiled four times with 360 c.c. of water for fifteen minutes each time; the residue is dried at 100° until the weight is constant.—*Helphenberg Annalen*.

Distinction between Articles of Silver and of Nickel.—The author uses a concentrated solution of silver nitrate. Genuine silver remains bright if moistened with the liquid; spurious articles turn black. Lacquer, if present, must first be rubbed off. The writer mentions, also, the 10 per cent solution of chromic acid. A drop of this liquid produces on silver a purple-red spot, but on other metals (except gold and platinum) a greyish black.

Sources of Error in the Assay of Gold and Silver.—Farman.—From the *Engineer and Mining Journal*.

Losses in the Cupellation of Bismuth-silver Alloys.—E. A. Smith.—From the *CHEMICAL NEWS*.

Determination of Silica in Blast-furnace Slags.—P. W. Shimer.—The author evaporates down with sulphuric and hydrofluoric acids.—*Journal of the American Chemical Society*.

Valuation of Manurial Matter containing Phosphoric Acid Insoluble in Water.—E. Wrampelmeyer (Landwirth Versuchsstationen).—There appear no characteristic differences between basic slag meals and phosphorites on treatment with a 5 per cent solution of citric acid and acid potassium oxalate.

Determination of Potassa in Manurial Salts.—V. Edwards.—From the *CHEMICAL NEWS*.

Determination of Yellow Phosphorus.—Jal. Föth (*Chemiker Zeitung*).—The author extracts with carbon disulphide until the extract, on shaking with silver nitrate, gives merely a faint brown colour.

Ferropyrin.—This is a proprietary medicine, made up by Knoll and Co., of 3 mols. of antipyrin and 1 mol. ferric chloride.

Recognition and Determination of Mercury in Urine.—A. Jolles.—The author uses metallic gold in the form of a powder in place of the materials previously used for amalgamation.—*Monatshefte für Chemie*.

Reaction for Acetacetic Acid in Urine.—K. A. H. Möner (*Skandinav. Archiv f. Physiologie*).—The urine is mixed with potassium iodide and ferric chloride. On boiling, a peculiarly irritating vapour is given off.

Determination of Glucose.—Lohnstein finds that the decrease of density on fermentation is not strictly proportional to the quantity of glucose.

Conditions of Solution of Uric Acid in Urine.—F. J. Smale (*Central-Blatt f. Physiologie*).—The author has obtained and examined saturated solutions of uric acid in water, in solution of sodium chloride, in solution of urea, and in solutions of disodium and monosodium-phosphate.

Detection of Urotilin, Jolles (*Pflüger's Archiv*); of hæmatoporphyrin in urine, Garrod (*Jour. of Physiologie*); and preservation of urinary sediments for microscopic examination (*Comptes Rendus*). We must refer to the originals.

Atomic Weights of Cerium, Didymium, Lanthanum, and some other Rare Elements.—P. Schützenberger (*Comptes Rendus*) has determined the atomic weight of cerium as 139.45. Brauner's method gave Ce=142—143. He gives the name meta-cerium to an element accompanying cerium and differing from it by a few spectral lines. Schützenberger calculates the atomic weight of didymium as 143—143.5. He succeeded in splitting up lanthanum into two earths having the respective atomic weights 138 and 135. From monasite he obtains the oxide of an earth forming salts of a full rose colour; its absorption spectrum corresponded to that of neodymium, and its atomic weight was close upon 137.5.

MISCELLANEOUS.

University of Edinburgh Chemical Society.—The second Ordinary Meeting of the above Society was held on Monday, December 14th. Dr. H. W. Bolam gave the Society an account of a research "On the Saponification of Dicarboxylglutaconic Ether" (see *CHEMICAL NEWS*, lxxiv., p. 278); a discussion took place after the paper had been read.

The Light Rays of the Firefly (Species?)—Prof. Muraoko, a Japanese *savant*, has communicated to Wiedemann's *Annalen* the results of some observations made on the light emitted by the firefly. He finds that this light, if transmitted through black paper, acquires properties similar to those of the X rays. Like the Becquerel, they are intermediate between the X rays and the ultra-violet. The firefly rays are capable of reflection, but whether they are susceptible of refraction, polarisation, and interference, it has not yet been demonstrated.

Cow Dung as a Cause of the Infection of Milk by Bacteria.—W. W. Favra.—The connection of cholera infantum with the bacteria of milk is demonstrated. Flügger has especially referred to twelve kinds of bacteria which he has isolated which occur in market-milk, one of which peptonises casein strongly; three of these species are strongly pathogenous. The author takes up the question of the introduction into considering the circumstance that, according to several investigations, from 3 to 19.7 m.grm. of impurities were found in milk which on microscopic examination are found to consist of particles of dung; there were instituted a series of bacteriological investigations of cow-dung. In 0.001 grm. there were found as many as 20,000 aerobic bacteria. The anaerobic species and those which do not grow upon agar-agar we disregarded. From seven to eight distinct species were recognised. The majority belonged to the ordinary intestinal bacteria; about 1½ per cent of all the bacteria were spores of peptonising bacteria. On a qualitative examination there were found four kinds of peptonising bacteria, I., VIII., IX., and XII. VIII. and XII. are especially of practical importance, as their spores are very persistent, and are not killed on boiling for four to five hours. The author believes therefore that cow-dung is one of the principal sources of the pollution of milk, especially on account of the peptonising and pathogenous bacteria.—*Wratsch*, 1896, xvii., 1114, and *Chemiker Zeitung*.

MEETINGS FOR THE WEEK.

TUESDAY, December 29th. } Royal Institution, 3. (Christmas Lec-
THURSDAY, December 31st. } tures). "Visible and Invisible
SATURDAY, Jan. 2nd, 1897. } Light," by Prof. S. P. Thompson.

Mr. J. G. LORRAIN, M.I.E.E., M.I.M.E., M.S.C.I.,
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INDEX.

- AACHEN**, Royal Technical High School at, 150
Aberdeen University, 138, 198
Aberystwyth, University College of Wales, 127
Abney, Capt., efficiency of a photographic shutter, 283
Absorbent, a quick nitrogen for the liberation of argon and the manufacture of metallic lithium, 6
Accidents, industrial, in Germany for 1895, 205
Acetacetic acid in urine, reaction for, 318
Acetal and monochloric acetal, 37
Acetanilide, alkaloidal reactions of, 62
Acetate, methyl, separation of ethylic alcohol from, 110
Acetic acid, recognition of mineral acids in presence of, 276
 separation of ethylic alcohol from, 110
 acids, chloric, ethylic ethers of the, 37
Acetobutyric acid, note on, 253
Aceton, determination of, 246, 265
Acetone and camphoric acid, compound of, 288
 relations of contraction on mixing with water, 293
"Acetylene and Its Applications. Incandescence by Gas and Petroleum" (review), 60
Acetylene, action of upon iron, nickel, and cobalt, 1
 explosive properties of, 209
 in air, detection of, 96
 limiting the explosive proportions of, 188
 on lighting with, 12
 conductivity of solutions of in water, 18
 explosion of with oxygen, 268
Acid, acetacetic, in urine, reaction for, 318
acetic, recognition of mineral acids in presence of, 276
 separation of ethylic alcohol from, 110
acetobutyric, note on, 253
acrylic, some derivatives of, 253
amidosulphonic, 277
 molecular conductivity of, 277
 physiological action of, 277
aspartic, rotation of, 105
blue nitrosulphonic, 49
nitrodisulphonic and its salts, various methods of formation of, 97
boric, role of in glasses and enamels, 306
camphoric, and acetone, compound of, 283
 remarks on the constitution of, 286
camphoronic, remarks on the constitution of, 286
camphorsulphonic, derivatives of, 288
Acid, carbonic, production of, 233
 rapid determination of in the air and in confined places, 64, 71
 chloride of, measure of heat of etherification, 37
 chlorofumaric, pyrazulone derivatives from, 252
chromic, bacterial action of, 184
 citrazinic, studies on, 253
 colloidal chromosulphuric, 121
 compounds of natural yellow colouring matters, 252
 constitution of inactive campholenic, 37
 cyanic, researches on, 121
 dichlorogallic, formation of, 49
 dimethylhexamethenylmalonic, experiments on the synthesis of, 279
 diokystearic, fission of, 12
 formic, determination of, 49
 evaporation heat of, 11
 gallic, reaction of, 283
 researches on the chloridation of, 49
 glutaric, some derivatives of, 253
 hydrofluoric, 36, 45
 in the gastric liquid, 99
 iodic, action of sulphuric acid and iodine upon, 293
 isanic, 49
 isopropylglutaric, 107
 ketonic, note on, 252
 levulic, volatility of, 121
 magenta S, distinctive character of ordinary magenta and of, on Schiff's reaction, 117
 metamidobenzoic, action of chloroform and potash on, 254
 nitric, in the waters of the Seine, the Yonne, and the Marne, 305
 nitrodisulphonic, deep blue, 34
 ortho-, meta-, and paraditoluytartaric, methylic and ethylic salts of, 105
 phenic, tempering steel with, 317
 phosphoric, a simplified method of determining by means of molybdc solution, 38
 and ether in presence of water, reactions between, 121
 colorimetric determination of in water, 45
 insoluble in water, manurial matter containing, 318
 table for calculating in magnesium phosphate, 110
 researches on, 292
 protocatechuic, reaction of, 283
 pyrophosphoric, determination of, 292
 transformation of, 292
 propionic, some derivatives of, 253
 salicylic, detection of saccharin in presence of, 49, 306
 selenic, preparation of, 85
Acid, soluble phosphoric, apparatus for extracting from superphosphates, 258
 some combinations of iodic with other acids, 84
sulphocamphoric, and derivatives of camphorsulphonic acid, 288
sulphocamphylic, 286
sulphuric, and iodine, action of upon iodic acid, 293
 determination of, 187, 246
 tartaric, and its alkaline salts, behaviour of with certain agents, 281
 detection of by means of resorcin, 276
thioacetic, use of in analysis in place of hydrogen sulphide, 73
uric, determination of in guano, 229
 fermentation of by micro-organisms, 84
 in 'urine, conditions of solution of, 318
 method for the determination of, 25
vanadic, reduction of by hydriodic and hydrobromic acids, 202
Acidic oxides, action of certain on salts of hydroxy-acids, 253
Acids, borax as an ultimate standard for, with methyl orange as indicator, 197
camphenesulphonic, derivatives of, 107, 279
 chlorobenzeneazosalicylic, the three, 106
 chloric acetic, ethylic ethers of the, 37
 complex fatty, on certain thiocarbimides derived from, 290
 dilute, absorption of by silk, 105
 ratio of solution of zinc in, 303
 fatty, electrolysis of, 85
 glyoxylic, of the aromatic series, action of hydrazines upon, 37
 hydriodic and hydrobromic, reduction of vanadic acid by, 202
 hydroxy, salts of, action of certain acidic oxides on, 253
 indoles and indol carbonic, recognition of, 109
 ketones and ketonic, condensation of halogen derivatives of fatty and ethereal salts with, 119
 ketonic, contributions to the knowledge of the, 252
 mineral, detection of in presence of organic acids, 49
 recognition of in presence of acetic acid, 276
monhydroxy, electrolysis of the salts of, 120
 new researches on the decomposition of sugars under the influence of, 233
Acids, organic, detection of mineral acids in, especially in vinegar, 49
 action of light on some in presence of uranium salts, 55, 67, 79
 oxybenzoic, and their derivatives, combination of anti-pyrine with, 11
 selenious and selenic, iodometric determination of, 3, 284
 sulphurous and sulphuric, determination of in products of combustion of coal-gas, 24
Aikman, C. M., R. P. Wright, and W. Fleischmann, "The Book of the Dairy" (review), 173
Ackroyd, W., action of metals and their salts on ordinary and Röntgen rays, 257
Aconitine, action of methyl alcohol on, 120
Aconitum heterophyllum, atisine, the alkaloid of, 120
Acrylic acid, some derivatives of, 253
Adiabatic relations of ethyl oxide, attempt to determine, 295
Admittance and impedance, 8
Africa, cattle plague in, 180
Agafonoff, M., absorption of the ultra-violet spectrum by crystalline substances, 196, 204
Agaricus atramentarius, analysis of air by, 292
Agricultural College, Royal, Cirencester, 130
 distilleries, report by M. Aimé Girard on the control of, 74
"Agricultural Experiment Station, Connecticut, Nineteenth Annual Report for 1895" (review), 84
Ahrens, C., and M. Dennstedt, determination of sulphurous and sulphuric acids in products of combustion of coal-gas, 24
Air, analysis of, by *Agaricus atramentarius*, 292
 by a mushroom, 247
 composition of, 292
 explosion and detection of acetylene in, 96
Pettenkofer's method for determining carbonic anhydride in, 287
 pumps, new mercurial, 25
 rapid determination of carbonic acid in, and in confined places, 64, 71
 detection and estimation of carbonic oxide in, 188
 presence of nitrites in, 230, 240
"Air, Detection and Measurement of Inflammable Gas and Vapour in" (review), 195
Alcohol, amyl, action of light on, 252
 and extract in wines, optical determination of, 25

- Alcohol, crotonylic, formation and etherification of, 85
ethyl, separation of from acetic acid, methyl ether, methyl acetate, aldehyds, phenols, &c., 110
methyl, action of on aconitine, 120
rational denaturation of, 37
sodic, measure of heat of etherification, 37
Alcoholates, aluminium, 53
Alcoholic liquors, action of oxygen upon, 184
Alcohols, methylic and ethylic, determination and separation of small quantities of, 110
colour of, compared with that of water, 182
polyatomic, and their derivatives, action of permanganate on, 317
"Alcohols, Industry of" (review), 317
Alcoylcamphors of the aromatic series, crystallographic properties of some, 85
Aldehyd, crotonic, reduction of, 73
formal, reactions of, 281
formic, action of water upon, 73
action of on phenylhydrazine, and hydrazones, 120
isobutyric, condensation products of, 12
Aldehyde, aromatic, new method for the preparation of, 49
glucose, and ketones, reactions for, 281
ozoniferous, for the detection of minimum traces of iodine in presence of chlorine and bromine, 7
separation of ethylic alcohol from, 110
Algae and bacteria, fixation of atmospheric nitrogen by the association of, 203
Alessandria, determination of phosphoric acid in water, 45
"Alkali, &c., Works Regulation Acts, 1881 and 1892" (review), 10
Alkalis, fixed, volumetric determination of the metals precipitable by, 109
mono- and bicarbonates of, volumetric estimation of, 116, 197
Alkalimetry, sources of error in, 172, 197
Alkaline earths, volumetric estimation of, 116, 197
metals, action of silicon upon, 73
sodium, potassium, lithium, dissociation-spectra of melted salts, 12
perchlorates, detection of in presence of chlorides, chlorates, and nitrates, 38
pyrogallol solution, determination of oxygen with, 199
Alkaloid of aconitine heterophyllum, 120
Alkaloidal reactions of acetanilide, 62
Alkaloids, new method for the quantitative isolation of, 246
iodine for volumetric determination of, 24, 246
Alkyl iodides, action of on silver malate, 290
and mercurous nitrite, interaction of 289
determination of combined with nitrogen, 49
Allen, A. H., "Commercial Organic Analysis" (review), 108
C. R., and H. C. Jones, conductivity of solutions of acetylene in water, 18
use of phenolphthalein in illustrating the dissociating action of water, 32
Allen, G. Y., and A. G. Perkin, colouring-matter of Sicilian sumach, *Rhus coriaria*, 120
Alloys and metals, solution and diffusion of in mercury, 289
antifriction, estimation of small amounts of bismuth in, 169
bismuth-silver, losses in the cupellation of, 318
metallic, 84
fusibility of, 73
aluminium, preparation of by a chemical reaction, 37
new method of preparing, 11
Aloy, J., thermic researches on uranium compounds, 49
Alum, chrome, effect of heat on aqueous solutions of, 278
Alumina and iron oxide in phosphate rock, determination of, 112, 146
determination of in phosphates, 399
in the ash of plants, 306
manufacture of at the works of Larne Harbour, 222
part played by in the production of glass, 12
Aluminium, action of mercury salts on, 30
silicon upon, 73
alcoholates, 58
alloys, preparation by a chemical reaction, 37
amalgam, 197
method for the separation of from iron, 296
chloride, action of upon benzene containing thiophene, 97
upon camphoric anhydride, 281
ethyloxalyl on naphthalene in presence of, 62
Allylene, preparation of, 78
Amanita muscaria, composition of red pigment of, 11
Amidosulphonic acid, 277
molecular conductivity of, 277
physiological action of, 277
Amines, primary, secondary, and tertiary, rapid determination of the components of a mixture of, 97
tertiary benzenoid, researches on, 303
Ammonia, action of upon potassium or sodium paratungstates, 84
and nicotine in tobacco, determination of, 185
determination of, 38
separation of trimethylamine from, 116
"Ammonia, the New Procedures for its Manufacture and its Applications" (review), 48
Ammoniacal derivatives of the phosphopalladous and phosphopalladic ethers, 233
nitrogen, occurrence of in primitive rocks, 64
Ammonium acetate method, determination of iron oxide and alumina in phosphate rock by, 112
molybdate solution, modified, 35
sulphate, technical determination of sulphocyanogen in, 317
Amyl alcohol, action of light on, 252
Amylene chain, structure of, 252
Analysis, elementary, with use of lead chromate, 110
new method of quantitative spectral, 258
introduction of standard methods of, 81, 89, 101, 118, 143, 159, 170
"Analysis, Inorganic Quantitative, Select Methods in" (review), 317
Analyst's Laboratory, Sheffield Borough, 138
Society of Public, 293
Analytical funnel, 257
Anatomic research, use of the X rays for, 270, 295
Anderson's College, Glasgow, 138
André, G., and M. Berthelot, determination of alumina in the ash of plants, 306
decomposition of sugars under the influence of acids, 233
reactions exerted between phosphoric acid and ether in presence of water, 121
researches on arabinose, 245
phosphoric acid, determination of pyrophosphoric acid, 292
volatility of levulinic acid, 121
transformation of pyrophosphoric acid, 292
Andrews, W. W., extensions of the plaster of Paris method in blowpipe analysis, 242, 247, 264, 272
Anethol, two isomers of, 62
Angeli, A., recognition of indoles and indol carbonic acids, 109
Angiology, use of X rays for, 295
Anhydride, camphoric, action of aluminium chloride upon, 281
carbonic, in air, Pettenkofer's method for determining, 287
"Animal and Microbian Toxines," by A. Gautier, 37
and vegetable oils in mineral oils, 62
Animals and plants, determination of iron in the ash of, 306
Aniline, double compounds of with metallic salts, 185
Anisol camphors, crystallographic properties of, 49
Anthracen, determination of, 50
Anti-coagulating substances, immunity conferred by, 196
Antimonite, 113
Antimony, action of silicon upon, 73
and iron, density and specific heat of alloys of, 85
separation of mercury from, 145
tetrachloride, action of nitrogen peroxide upon, 61
Antipyrin, combination of with oxybenzoic acids, 11
Apparatus, new sulphuretted hydrogen, 25
extraction, 25
for fractionated distillation, 25
new, 25
Apatite, plumbiferous, 113
Apatites, variations observed in the composition of, 12
Apple rings, zinc in American, 49
Appiepard, J. R., and J. Walker, absorption of dilute acids by silk, 105
"Applied Bacteriology" (review), 207
"Applied Science, Catalogue of Case School of" (review), 255
Aqueous solutions of chrome-alum, effect of heat on, 278
Arab-nose, researches on, 246
Arable soils, nitrogen in, 110
Arcowski, H., solubility of solids in gases, 194
Areca nut, poisoning by, 295
Argentiferous lead, electrolytic disargeneration of, 37
desilvering, 40
Argon and helium, 179, 209, 260
homogeneity of, 75, 85, 209
and nitrogen in fire-damp and in the Rochebelle gas, 87, 97
study on, 85, 100
quick nitrogen absorbent for liberation of, 6
combination of with water, 122
densities of, 292
helium, and Prout's hypothesis, 223
uniformity of distribution, 270
Armbruster, L., adjustment and suspensions for terminal knife-edges of balances, 25
Armstrong, H. E., bromo-naphthol, 301
notes on nitration, 301
studies of the terpenes and allied compounds, note on ketopinic acid, 252
Aromatic aldehyds, new method for the preparation of, 49
Aromatic series, crystallographic properties of some alcoylcamphors of the, 85
Arsenate of lead, a new insecticide, 17
Arsenic, separation of mercury from, 145
Asbestos covers, iron-wire nets with, 257
Ash in commercial milk sugar, 50
of plants and animals, volumetric determination of iron in, 306
alumina in, 306
Aspartic acid, rotation of, 105
Aspirator, use of Geissler filter-pump as an, 230
Assay, copper, by the iodide method, 52
of gold and silver, sources of error in, 318
Atisine, the alkaloid of aconitine heterophyllum, 120
Atomic motion of the elements, 53
weight of molybdenum, 62
of yttrium, re-determination of, 62
weights of cerium, didymium, lanthanum, and some other rare elements, 318
of simple substances, succession of, 233, 260
Atoms, form of, 168
Atmosphere, ozone in, 180
Atmosphere, composition of, 292
nitrogen, fixation of by association of algae and bacteria, 293
Atramentarius agaricus, analysis of air by, 292
Auchy, G., sources of error in Volhard's and similar methods of determining manganese in steel, 214, 248, 262
Aufschläger, H., behaviour of nitrogenous organic bodies with potassium polysulphides, 186
Austen, P. T., chemists as leaders, 178
Autenrieth, W., luteol, a new indicator, 25
Auto-pneumatic stirrer, 63
Avery, S., and H. H. Nicholson, electrolytic determination of iron, nickel, and zinc, 91
Aymonnet, M., periodic maxima of spectra, 246
BACH, A., reduction of nitrates and formation of quaternary nitrogenous matters in plants, 37
Bacillus of diphtheria, action of Röntgen rays upon, 73
prodigious, reactions of the pigment of, 62
Bacteria and algae, fixation of atmospheric nitrogen by association of, 293
cow dung as a cause of the infection of milk by, 318
Bacterial action of potassium permanganate, chromic acid, and iodine, 184
Bactericidal power of the blood, increase of, 196
Bacteriological examination and chemical analysis of potable water, 73
"Bacteriology, Applied" (review), 297
Baedtker, E., action of aluminium chloride upon benzene containing thiophene, 97
Bailey, G. H., volatilisation of salts during the evaporation of water, 258
Baker, H. B., and H. B. Dixon, chemical inactivity of Röntgen rays, 121
Balance, chemical, substitute for, 257
Balances and weights, 25
adjustment and suspensions for terminal knife-edges of, 25
Ball, J., circumstances which affect the ratio of solution of zinc in dilute acids, 333

- Balland, M., nutritive value of flours, and economic consequences of excessive sifting, 38
on beans, 210
- Balloons, scientific explorations in, 305, 317
- Balsam of copaiva, recognition of fatty oils in, 110
- of Peru, examination of, 110
- Bangor, University College of North Wales, 127
- Barbet and Jaudrier, MM., detection and determination of nitrites in water, 222
- Barbier, P., and L. Bouveault, synthesis of natural methylheptenone, 12
- Barium dinickelate, nickel dioxide, properties of, 196
determination of, 187
sulphate, solubility, 109
- Barklyite, 114
- Barley straw, carbohydrates, 267
- Barometer for the laboratory, 258
- Barr, J. M., and G. G. Henderson, action of certain acid oxides on salts of hydroxy acids, 253
- Barrell, F. R., G. L. Thomas, and S. Young, separation of three liquids by fractionated distillation, 258
- Barrière, P., lutium, a new element, patented, 212
- Barton, Dr., and Mr. Bryan, absorption of electrical waves along wires by a terminal bridge, 254
- Baryta tube, new, 246
- Bassett, H., determination of anthraxen, 50
- Battersea Polytechnic, 137
- Baumann, A., gas-volumetric determination of free iodine, 109
J., and W. Horn, vacuum water bath, 197
- Beadle, C., and A. Little, new derivative of cellulose, 12
- Beans, 210
- Beaulard, F., non-refraction of the X rays by potassium, 97
- Beck, C. R., hot-water funnel, 257
- Bequerel, H., various properties of the uranic rays, 305
- Bedell, F., admittance and impedance, 8
- Beebe, A. C., chemical education in England and Germany, 245
- Beer wort, quantitative separation of the proteid substances present in, 185
- Béhal and Guerbet, MM., constitution of inactive campholenic acid, 37
- Behrens, H., micro-chemical analysis of organic compounds, 38
micro-chemical distinction between cinchonidine and hocinchonidine, 109
- Belahoubek, A., and Sedlecky, the thallioquin reaction, 100
- Belar, A., examination of red wines for foreign colouring matters, 196
- Belfast, Queen's College, 135
- Belgium, chicory in, 306
- Benedikt, Hr., analysis of fats, oils, and waxes, 50
- Benoist, L., electroscope with three gold leaves, 84
- Bentley, W. H., and W. H. Perkin, acetobutyric acid, 253
- Benzoacetic, methyl, formation of, 120
- Benzene, action of nascent bromine upon, 109
containing thiophene, action of aluminium chloride upon, 97
determination of thiophen in, 50
- Benzenoid amines, tertiary, researches on, 303
- Benzdin, and toluidin, valuation of, 109
- Benzoyl radicle, detection of in organic substances, 276
- Benzylidene, methyl- and ethyl-salicydenes and anisol camphors, crystallographic properties of, 49
- Bergamot, oil of, determination of purity of, 25, 246
- Berthelot, M., copper mines of Sinai, 121
researches on cyanic acid, 121
and G. André, alumina in the ash of plants, 306
reactions exerted between phosphoric acid and ether in presence of water, 121
researches on arabinose, 246
decomposition of sugars under the influence of acids, 233
determination of pyrophosphoric acid, 292
volatility of levulic acid, 121
transformation of pyrophosphoric acid, 292
and Vieille, MM., explosive properties of acetylene, 209
- Berton, P., action of the Röntgen rays upon the bacillus of diphtheria, 73
- Bertram, J., and H. Walbaum, oil of seseda root, 74
- Bertrand, G., simultaneous presence of laccase and of tyrosinase in the juice of certain fungi, 174
- Beryl, 114
- Besson, A., action of certain hydrogen compounds upon thionyl chloride, 306
- Beswick Technical Institute, 138
- Bevan, E. J., C. F. Cross, and C. Smith, carbohydrates of barley straw, 267
- Beverages, detection of dulcin in, 48, 306
- Bibliography of spectroscopy, 222
- Bicarbonates of the alkaline earths, alkalis, and magnesia, volumetric determination of, 116, 197
- Biétrix, A., researches on the chloridation of gallic acid, 49
- Bigelow, W. D., and K. P. McElroy, determination of cane-sugar in presence of milk-sugar, 293
- Biltz, H., glass vessels for preserving substances sensitive to light, 25
- Binodate, potassium, 197
- Biological chemistry and mechanics, 97
- Birkbeck Literary and Scientific Institution, 137
- Birkeland, M., spectrum of the cathodic rays, 196
- Birmingham, Mason College, 129
- Bismuth, action of silicon upon, 73
estimation of small amounts of in anti-friction alloys, 169
oxyiodide, 200
separation of from the metals of the copper and the iron group, 162
silver alloys, losses in cupellation of, 318
sulphide, solubility of in sodium sulphide, 169
- Blair, A. A., "The Chemical Analysis of Iron" (review), 255
- Blake, R. F., and Prof. Letts, Pettenkofer's method for determining carbonic anhydrides in air, 287
- Blanc, G., action of aluminium chloride upon camphoric anhydride, 281
- Blast-furnace slags, determination of silica in, 318
- Blood, increase of the bactericide power of, 196
new ferment in, 281
- Blowpipe analysis, extensions of the plaster of Paris method in, 242, 247, 264, 272
electric, 281
- Blue dye obtained from quinone, 236
nitrosulphonic acid, and its salts, various methods of formation, 49, 97
- Blyth, T. R., bismuth oxy-iodide, 200
- Body having a negative resistance, properties of, 8
- Bolam, H. W., hydrolysis of ethylic dicarboxylglutamate, 278
- Bondsept, A., system of gas-burners, report by M. Violle, 12
- Bone, W. A., and J. C. Cain, explosion of acetylene with oxygen, 268
and D. S. Jerdan, direct union of carbon and hydrogen, 263
- Borax as an ultimate standard for acids, with methylorange as indicator, 197
- Bordas and Génin, MM., congelation-point of cows' milk, 161
- Boric acid, role of in glasses and enamels, 306
- Bornträger, A., determination of the purity of oil of bergamot, 25, 246
H., dissolving iron and other metallic oxides, 9, 109
- Boron, commercial preparation of, 64
- Bose and Delezenne, MM., immunity conferred by some anti-coagulating substances, 196
J. C., farewell banquet to at Bombay, 198
- Bottle with liquid joint, 25
- Bottomley, J. T., Lord Kelvin, and M. Maclean, measurement of electric currents through air of different densities, 175
- Boucher, G. G., estimation of sulphur in cast iron or steel, 76
- Boudouard, M., and P. Schützenberger, earths of the yttria group contained in monasite sands, 292
- Bougault, J., action of sulphur chloride upon pentaerythrite, 84
- Bouillhae, R., fixation of atmospheric nitrogen by association of algae and bacteria, 293
- Bourquelot, E., action of the soluble oxidising ferment of mushrooms upon phenols insoluble in water, 161
- Bouveault, L., action of hydrazines upon the glyoxylic acids of the aromatic series, 37
new method for the preparation of aromatic aldehyds, 49
and P. Barbier, synthesis of natural methylheptenone, 12
- Bradford Technical College, 130
- Braithwaite, ash in commercial milk-sugar, 50
- Brauner, B., action of hydrogen sulphide upon cupric salts, 99
argon, helium, and Prout's hypothesis, 223
- Brazil, diamantiferous sands of, 97
- Brazilian and Carolina monazite, 74
- Bread, alimentary value of from flours sifted to different standards, 7, 12
- Brearley, H., auto-pneumatic stirrer, 63
estimation of nickel in steel, 16
- Breckenridge, J. E., and D. A. Kreider, separation and identification of potassium and sodium, 227
- Brewer, chemical laboratory of the, 50
- Bristol, Clifton Laboratory, 137
University College, 128
- British Association, Chemical Section, 161
Liverpool Meeting, inaugural address, 139, 151
address to the Chemical Section, 156, 163
- British flint-glass trade, 193
plants, colouring-matters occurring in various, 278
- Brizard, L., action of reducing agents upon nitroso-compounds of osmium, 84
- Bromal and chloral hydrates, 95
- Bromide, ferrous, absorption of nitric oxide by, 317
- Bromides, researches on the double, 196
- Bromine and chlorine, ozoniferous aldehyds for the detection of iodine in presence of, 7
and iodine, replacement of chlorine by, 27
action of on pinene, with reference to the question of its constitution, 94
determination of chlorine in, 25
nascent, action of upon benzene, 109
behaviour of naphthols and naphthylamines with, 109
- Bromo-naphthol, 301
- Brooks, C. J., refrigerator for distillations from a test-glass, 257
- Brown, A. C., the life and work of Kekulé, 201
- Browne, F., Japanese coal, 76
- Browning, P. E., reduction of vanadic acid by hydriodic and hydrobromic acids, 202
and L. C. Jones, estimation of cadmium as the oxide, 190
- Brucine, certain colour reactions of, 233, 240
- Bryan and Barton, Messrs., absorption of electrical waves along wires by a terminal bridge, 254
- Buckwheat and ground rice, distinction between, 50
- Buguet, A., Röntgen's phenomenon, 270
- Bunsen burner, new, 197
with a safety-basket of wire-netting, 257
- Burgess, H. E., and A. C. Chapman, santal and some of its derivatives, 95
W. T., taking samples of water for bacteriological purposes, 258
- Butter, cacao, iodine number and index of refraction of, 109
cocoa, the iodine number of, 236
digestibility of cocoa-nut butter and cows', 233
- Byrant, E. G., Geissler filter-pump as an aspirator, 230
- CACAO butter, iodine number and index of refraction of, 109
- Cadmium, estimation of as the oxide, 190
- Cain, J. C., and W. A. Bone, explosion of acetylene with oxygen, 268
- Cafr-Mantrand, M., separation of ethyl alcohol from acetic acid, methylic ether, methyl acetate, aldehyds, phenols, &c., 110
- Calcium, silicide of, 33
- "Calendar for the Year 1896-7, University College of North Wales" (review), 256
- Calvert, H. T., and T. Ewan, colloidal chromsulphuric acid, 121
- Cambridge, University of, 124
- Cameron, Sir Chas., 217
- Camphene-sulphonic acids, derivatives of, 107, 279
- Campholenic acid, inactive, constitution of, 37
- Camphor, halogen derivatives of, 279
- Camphoric acid and acetone, 283
constitution of, 246
anhydride, action of aluminium chloride upon, 281
mononitrile, its anhydride and its anilide, 85
- Camphoronic acid, constitution of, 286

- Camphors, crystallographic properties of benzylidene, methyl- and ethyl-salicydenes, and anisol, 49
- Camphorsulphonic acid, derivatives of, and sulphocamphoric acid, 258
- Camphoroxime, new base derived from, 104
- Canada balsam, oil, &c., cleansing port objects from, 258
- Cane-sugar in presence of milk-sugar, determination of, 293
- Cap composition, analysis of, 283
- Capillary affinities, study of, 11
- Caramel, detection of in wines, 306
- Carbide, lanthanum, study of, 284
- Carbides, classification of, 37
- metallic, formation of hydrocarbides by action of water on, 37
- researches on, 15
- Carbohydrates, colorimetric determination of, 293
- of barley straw, 267
- of cereal straws, constitution of, 177
- Carbon and hydrogen, direct union of, 268
- dioxide, iodometric method for determination of, 65
- solubility of in rhodium, iridium, and palladium, 61
- tetrachloride, reaction between and oxides of niobium and tantalum, 33
- Carbonates and hydroxides, volumetric determination of, 116, 197
- Carbonic acid, indol, recognition of, 109
- production of, 233
- rapid determination of in the air, 64, 71
- anhydride in air, Pettenkofer's method for determining, 287
- oxide in the air, detection and estimation of, 188
- Cardiff, University College of South Wales, 128
- Carnot, A., variations in the composition of apatites, 12
- Carolina and Brazilian monazite, 74
- Cartvale Chemical Co., "Inquiry into the Alleged Liability of Wood Charcoal to Spontaneous Combustion" (review), 61
- "Case School of Applied Science, Catalogue of" (review), 255
- Cast-iron or steel, estimation of sulphur in, 76, 257
- Castell-Evans, J. "A New Course of Experimental Chemistry" (review), 256
- Catalogue conference, international, 58
- "Catalogue of Case School of Applied Science," 255
- Catholic University, Dublin, 138
- Cattle plague in Africa, 180
- Cavalier, J., measure of heat of etherification, 37
- Caviere, examination of, 49
- Cazeneuve, P., distinctive character of ordinary magenta and of acid magenta S on Schiff's reaction, 117
- "Celluloid, Fulminates, and Smokeless Powders—Nitro-Explosives" (review), 23
- Celluloid, funnel, 257
- Cellulose, a filter of, 98
- new derivative of, 12
- Central School of Chemistry and Pharmacy, 137
- Cementated steels, 5
- Cereal straws, constitution of the carbohydrates of, 177
- Cereals, determination of starch in, 306
- Ceria and thoria, separation of, 257
- Cerium, atomic weight of, 318
- Chapman, A. C., and H. E. Burgess, santal and some of its derivatives, 95
- Charabot, E., and G. Chiris, essential oil of resin, 281
- Charon, E., formation and etherification of crotonyl alcohol, 85
- reduction of crotonic aldehyd, 73
- Chatelier, H. le, curves of solubility, 233
- Chattaway, F. D., constitution of nitrogen iodide, 267
- Chauveau, A., biological chemistry and mechanics, 97
- nature of the chemical process which governs the transformation of the potential from which the muscles derive the energy necessary for work, 11
- Cheese, chemical examination of, 257
- Cheever, B. W., and F. C. Smith, "Select Methods in Inorganic Quantitative Analysis" (review), 317
- Chelsea, South West London Polytechnic Institute, 150
- "Chemical Analysis, Elementary Quantitative (review), 173
- "Chemical Analysis of Iron" (review), 255
- "Chemical Apparatus, &c., and Chemicals, Catalogue of" (review), 148
- "Chemical Lecture Experiments" (review), 256
- "Chemical Notes and Equations" (review), 24
- Chemical and bacteriological examination of water, 73
- balance, substitute for, 257
- education in England and Germany, 175, 245
- examination of cheese, 257
- laboratory, an ideal, 312
- of the brewer, 50
- Wiesbaden, 112
- practical use in of the electric arc obtained from the low potential alternating current, 92
- literature, fourteenth annual report of the committee on indexing, 111
- Section of the British Association, 161
- address to, 156, 163
- Society, 94, 104, 119, 251, 266, 277, 286, 300, 316
- Edinburgh University, 291, 318
- Technology, Institute of, Liverpool, 137
- Chemistry and Pharmacy, Central School of, 137
- Westminster College of, 137
- biological, and mechanics, 97
- forensic, contributions to, 120
- national value of, 174
- of phenol derivatives, 251
- the constituents of monazite, 274
- "Chemistry, A Junior Course of Practical" (review), 281
- "Chemistry at a Glance" (review), 72
- "Chemistry, Elementary Practical, and Qualitative Analysis" (review), 71
- "Chemistry, Experimental, a New Course of" (review), 256
- "Chemistry for Beginners" (review), 208
- "Chemistry of the Metals, a Tabular Atlas of the" (review), 185
- "Chemistry, Practical" (review), 209
- Chemists as leaders, 178
- Chicory in Belgium, 306
- Chikashigé, M., atomic weight of Japanese tellurium, 106
- Chiris, G., and E. Charabot, essential oil of resin, 281
- "Chile, Hygienic Review of" (review), 280
- "Chile, General Scientific Congress, 1894" (review), 149
- "Chilian Review of Hygiene" (review), 61
- Chloral and bromal hydrates, 95
- condensation of with resorcinol, 106
- Chlorate, potassic, and manganic peroxide, liberation of chlorine during heating of a mixture of, 95
- Chlorated ethers, 12
- Chlorates, chlorides, and nitrates, detection of alkaline perchlorates in presence of, 38
- Chloric acetic acids, ethylic ethers of, 37
- Chloridation of gallic acid, 49
- Chloride, aluminium, action of upon benzene containing thiophene, 97
- ethyloxalyl on naphthalene in presence of, 62
- upon camphoric anhydride, 281
- of acid, measure of heat of etherification by the action of upon sodic alcohol, 37
- sulphur, action of upon penterythrite, 84
- stannous, action of iodine upon, 49
- thionyl, action of certain hydrogen compounds upon, 306
- Chlorides, chlorates, and nitrates, detection of alkaline perchlorates in presence of, 38
- double, 161
- metallic, action of phosphorus on certain, 37
- of the non-metals and metalloids, replacement of chlorine in by bromine and iodine, 27
- Chlorine and bromine, detection of traces of iodine in presence of, 7
- determination of inorganic products, 109
- in bromine, determination of, 25
- replacement by bromine and iodine, 27
- liberation of during the heating of a mixture of potassic chlorate and manganic peroxide, 95
- Chlorobenzeneazosalicylic acids, the three, 106
- Chloroform and potash, action of on metamidobenzoic acid, 254
- Chlorotumaric acid, formation of pyrazolon derivatives from, 252
- Chlorophylls, spectrum of the, 293
- Chloroplatinates, volumetric determination of, 38
- Chree, C., applications of physics and mathematics to seismology, 304
- Chretien, P., action of sulphuric acid and iodine upon iodic acid, 293
- some combinations of iodic acid with other acids, 81
- Chromate, lead, elementary analysis with the use of, 110
- Chrome alum. effect of heat on aqueous solutions of, 278
- Chronic acid, bacterial action of, 184
- Chromite, magnesium, 306
- Chromsulphuric acid, colloidal, 121
- Chrysocolia, 114
- Cigarettes, tea, 143
- Cinchonidine and hocinchonidine, micro-chemical distinction between, 109
- Cinnabar, electrolytic method for the determination of mercury in, 310
- Cirencester, Royal Agricultural College, 130
- Citrazinic acid, 253
- City and Guilds of London Institute, 57, 136, 236
- of London College, 137
- School, jubilee of science teaching in, 216, 269
- "City and Guilds of London Institute, A short History of" (review), 72
- Clarke, T., and F. P. Venable, study of the zirconates, 42, 54
- Clarke, F. W., empirical relation between melting-point and critical temperature, 101
- Clèveite gas, new elements of, 238
- Clifton Laboratory, Bristol, 137
- Cloves, adulterated, starch and ethereal oils in, 49
- Clowes, F., explosion and detection of acetylene in air, 96
- limiting the explosive proportions of acetylene, 188
- determination of oxygen by absorption with alkaline pyrogallol solution, 199
- carbonic oxide in the air, 188
- "Detection and Measurement of Inflammable Gas and Vapour in the Air" (review), 195
- and J. B. Coleman, "Elementary Practical Chemistry and Qualitative Analysis" (review), 71
- "Elementary Quantitative Analysis" (review), 173
- Coal dust, 51
- gas, sulphurous and sulphuric acids in products of combustion of, 24
- Japanese, 76
- proximate constituents of, 261, 271, 292, 305
- Cobalt, action of haloid compounds of phosphorus upon, 84
- and nickel, new salts of, 212
- atomic weight of, 110
- action of acetylene upon, 1
- Cobaltite, magnesium, 85
- Cochenhausen, F. v., valuation of wool-fat, 62
- Cocks, glass, with safety arrangement, 25
- Cocount butter iodine number of, 236
- and cows' butter, comparative digestibility of, 233
- Cohn, L., ether, 25
- Coleman, J. B., and F. Clowes, "Elementary Quantitative Analysis" (review), 173
- "Elementary Practical Chemistry and Qualitative Analysis" (review), 71
- College, Anderson's, Glasgow, 138
- Bradford Technical, 130
- City of London, 137
- Firth, Sheffield, 133
- Glasgow Veterinary, 138
- Heriot-Watt, Edinburgh, 134
- King's, 125
- Mason, Birmingham, 129
- of Chemistry and Pharmacy, Westminster, 137
- of Science, Durham, 131
- for Ireland, Royal, 136
- Royal, and Royal School of Mines, 126
- of Surgeons in Ireland, Royal, Dublin, 138
- Owens, Manchester, 134
- Queen's Belfast, 135
- Cork, 136
- Galway, 136
- Royal Agricultural, Cirencester, 130
- Technical, Glasgow and West of Scotland, 135
- Trinity, Dublin, 125
- University, 125
- Bristol, 128
- Dundee, 134
- Liverpool, 130
- Nottingham, 133
- of Wales, Aberystwyth, 12
- of North Wales, Bangor, 127
- of South Wales, and Monmouthshire, Cardiff, 128
- Tutorial, 137
- Yorkshire, Leeds, 130
- "College, University, of North Wales, Calendar for 1896-7" (review), 256
- Colleges and universities, 123
- Collie, J. N., appointment, 13
- and W. Ramsay, homogeneity of argon and helium, 75, 83, 209

- Colloidal chromsulphuric acid, 121
- Colorimetric determination of carbohydrates, 293
- phosphoric acid in water, 45
- Colour and constitution, 300
- photography, 275, 285
- reactions of saffron and its adulterants, 306
- Coloured indicators and salts, neutrality of, 285
- Colouring matters, acid compounds of natural yellow, 252
- Lefevre's treatise on, 74
- matter in the bark of *Myrica nagi*, 104
- in British plants, 278
- power of litmus, 297
- Colours, dyed, action of light upon, 205, 218
- Colson, R., action of zinc upon a photographic plate, 61
- Combes, C., preparation of alloys of aluminium by a chemical reaction, 37
- "Commercial Organic Analysis" (review), 108
- Commercial starches, 306
- Condensation products of isobutyric aldehyd, 12
- "Connecticut Agricultural Experiment Station, Report for 1895" (review), 84
- Congelation point of cows' milk, 161
- Conrad, A., reagent for sugar, 276
- Constants, refraction, of crystalline salts, 268
- Constitution and colour, 300
- Contremoulins and Remy, MM., cranial endography by means of the Röntgen rays, 85
- use of the X rays for anatomical research, 270, 295
- Cook, E. H., poisoning by areca nut, 295
- Copaiva, balsam, fatty oils in, 110
- Copper and iron group, separation of bismuth from, 162
- assay by the iodide method, 52
- electrolytic separation of, 50
- mines of Sinai worked by the ancient Egyptians, 121
- ores, roasted, sulphur in, 62
- separation of mercury from, 145
- sulphide, reduction of, 18
- Cotton seeds, 196, 221, 231
- Cow dung as a cause of the infection of milk by bacteria, 318
- Cows and coconut butter, comparative digestibility of, 233
- milk, congelation-point of, 161
- Cranial endography by the Röntgen rays, 85
- Cresol, crude, valuation of, 62
- Critical temperature and melting point, relation between, 101
- Crocoisite, 114
- Crookes, W., construction of the slit of spectroscopes, 258
- effect of molecular bombardment on the diamond, 39
- the alleged new element, lucium, 259
- and J. Dewar, London water supply, 41, 88, 169, 207, 266, 313
- Cross, C. F., and E. J. Bevan, proximate constituents of coal, 292
- and C. Smith, carbohydrates of barley straw, 267
- carbohydrates of cereal straws, 177
- Crotonic aldehyd, reduction of, 73
- Crotonylic alcohol, formation and etherification of, 85
- Crucible steels, phosphorus and sulphur in, 76
- substances, absorption of the ultra-violet spectrum by, 196, 204
- Crystallographic properties of benzylidene, methyl- and ethyl-salicylenes and anisol camphors, 49
- some alcoyl camphors of the aromatic series, 85
- Crystallography of the mono-hydrated mercurous nitrite, 289
- Cupellation of bismuth-silver alloys, losses in the, 318
- Cupric salt solutions, action of hydrogen sulphide on, 99
- Cupriferous pyrites, determination of sulphur in, 62
- Cuprous compounds for the recognition of the nitrites, 6
- Curves of solubility, certain peculiarities of, 233
- Cyanamide, thermic researches on, 222
- Cyanoic acid, researches on, 121
- "Cyanide Process of Gold Extraction" (review), 195
- Cyanides, double, 73
- "Cycling as a Cause of Heart Disease" (review), 305
- DAFERT, W., determination of nitrogen in arable soils, 110
- "Dairy, The Book of the" (review), 173
- Davis, W. A., derivatives of nitronaphthols, 302
- morphotropic relations of naphthol derivatives, 302
- De Brevans, J., "Les Conserves Alimentaires" (review), 10
- De Chalmot, G., silicide of calcium, 33
- De Grammont, A., dissociation-spectra of melted salts, 12
- direct spectroscopic examination of minerals and fused salts, 258
- spectrum of phosphorus in fused salts, 41, 49
- spectra of the non-metals in melted salts, 11
- De Koninck, L. L., estimation of sulphur in ores, 224
- extraction apparatus, 258
- De Lannoy, S., expansion of water on change of temperature, 258
- De Luynes, M., report on M. Lefevre's treatise on colouring-matters, 74
- Delafontaine, M., and C. E. Linebarger, reaction between carbon tetrachloride and the oxides of niobium and tantalum, 33
- De la Rozière, W., vegetable and animal oils in mineral oils, 62
- Deeley, R. M., the periodic law, 278
- Defacqz, E., compounds of tungsten, 88, 97
- separation of tungsten from titanium, 293
- Defren, G., nitrites in the air, 230, 240
- Dehéran, P. P., and E. Demoussy, oxidation of the organic matter of the soil, 97
- Delacré, M., pinacoline, 85
- Delaunay, M., atomic weights of simple bodies, 233, 260
- Delépine, M., action of water upon formic aldehyd, 73
- hexamethylenamine and some of its derivatives, 246
- salts of, 306
- preparation of methyl nitrate, 12
- Delezenne and Bose, MM., immunity conferred by some anti-coagulating substances, 196
- Deligny, M., and C. Matignon, nitro-substitutions, 12
- Demoussy, E., and P. P. Dehéran, oxidation of the organic matter of the soil, 97
- Denigès, G., milk sugar, 49
- detection of tartaric acid by resorcin, 276
- Dennis, L. M., separation of thorium from the other rare earths by potassium trinitride, 314
- and A. E. Spencer, zirconium tetraiodide, 102
- Dennstedt, M., and C. Ahrens, sulphurous and sulphuric acids in products of combustion of coal-gas, 24
- Dephlegmator, 258
- Desilvering argentiferous lead, electrolytic, 40
- Development, use of X rays for, 295
- Dewar, J., and W. Crookes, London water supply, 41, 88, 169, 207, 266, 313
- Dextrose, identity of from different sources, 289
- Diamantiferous sands of Brazil, 97
- Diamond, W., filter flask, 283
- Diamond preparation of, 85
- effect of molecular bombardment on, 39
- study of the black, 85
- Diamonds, steel, 73
- Dibenzoyl and ditolyl tartrates, comparative rotatory powers of, 279
- Dicarboxylglutamate, ethylic, hydrolysis of, 278
- Dichlorogallac acid, formation of, 49
- Didymium, atomic weight of, 318
- Dierbach, K., Bunsen burner, 197
- Dielectric, in the discharge of Röntgen's rays, 121
- Dieterich, E., colouring power of litmus, 297, 317
- insoluble residue in isinglass, 318
- examination of olive oil, 74
- Dilute solutions, refractive power and density of, 25
- Dimethylhexamethenylmalonic acid, synthesis of, 279
- Dimethylketohexamethylene, preparation of, 279
- Dinickelite, barium, nickel dioxide, existence and acid properties of, 196
- Dioxide, carbon, iodometric method for determination of, 65
- nickel, barium dinickelite, existence of, 196
- Dioxysearic acid, fission of, 12
- Diphenyliodonium and thallium nitrates, isomorphism of, 217
- Diphtheria, action of the Röntgen rays upon the bacillus of, 73
- Disinfective preparations and soaps, phenol in, 197
- Distillation, fractionated, apparatus for, 25
- separation of three liquids by, 258
- "Distillation, Industry of" (review), 317
- Distillations from a test-glass, refrigerator for, 257
- Distilleries, agricultural, report of M. Aimé Girard on the control of, 74
- "Distillery, Treatise on" (review), 317
- Ditolyl tartrates and dibenzoyl, rotatory powers of, 279
- Divers, E., and T. Haga, amidosulphonic acid, 277
- economical preparation of hydroxylamine sulphate, 269
- imidosulphonates, 269
- reduction of nitrosulphates, 269
- Dixon, A. E., thiocarbinides derived from fatty acids, 290
- H. B., and H. B. Baker, chemical inactivity of Röntgen rays, 121
- Dobriner, P., and W. Fresenius, determination of sugars, 197
- Doelter, C., behaviour of Röntgen rays, 39
- Dommer, F., "Incandescence by Gas and Petroleum, Acetylene and its Applications" (review), 60
- Double silicates of potassium and other bases, reproduction of, 270
- Dougal, M. D., effect of heat on solutions of chromalum, 273
- Drossbach, P., chemistry of the constituents of monasite, 274
- Duboin, A., reproduction of double silicates of potassium and other bases, 270
- Ducrétet, E., and L. Lejeune, cock for receivers for compressed gases, 292
- Dufau, E., crystalline neutral magnesium chromite, 306
- magnesium cobaltite, 85
- existence and acid properties of nickel dioxide, barium dinickelite, 196
- and G. Patein, combination of antipyrine with the oxybenzoic acids, 11
- Dulcin, detection of in beverages, 48, 306
- Dunstan, W. R., T. Tickle, and D. H. Jackson, action of methyl alcohol on aconitine, formation of methyl benz-aconine, 120
- Dupont, J., and J. Guerlain, essential oil of roses, 270
- Durkee, F. W., oxidation of sodium sulphide and hydrosulphide by electrolysis, 70, 80
- Dussy, J., specific heat of sulphur in the state of viscosity, 97
- Dye, blue, from quinone, 235
- Dyed colours, action of light upon, 205, 218
- EARTH, alkaline, mono- and bi-carbonates of, 197
- Earths of the yttria group in the monasite sands, 292
- Edinburgh University Chemical Society, 291, 318
- Edington, D., cattle plague in Africa, 180
- Edmunds, J., determination of sulphuric acid, 246
- or of barium, 187
- Education, chemical, in England and Germany, 175, 245
- Edwards, A. H., celluloid funnel, 257
- V., potassa in manurial salts, 318
- W. B., and F. S. Kipping, preparation of dimethylketohexamethylene, and synthesis of dimethylhexamethenylmalonic acid, 279
- Effront, M., report on the labours of, 12
- Egyptians, ancient, copper mines of Sinai worked by, 121
- Electric arc, practical use in the chemical laboratory of, 92
- blowpipe, 281
- conviction produced by Röntgen's rays, 149
- currents, measurement of through air of different densities, 175
- effluve, action of on the property of gases to discharge electrified bodies, 233
- Electrical waves, absorption of along wires by a terminal bridge, 254
- Electricity, heating by, 258
- Electrified bodies, discharge of by the X rays, 174
- substances, manner in which the X rays occasion the discharge of, 73
- Electro-catalytic action of boron, 64
- chemical production of metallic sulphides, 191
- Electrolysis of fatty acids, 85
- salts of mono-hydroxy acids, 120
- oxidation of sodium sulphide and hydrosulphide, 70, 80
- Electrolytes having a common ion, conductivity of mixtures of, 21, 35, 44
- Electrolytic conductivity, measuring, 232
- disargeneration of argentiferous lead, 37, 40
- determination of iron, nickel, and zinc, 91
- separation of copper, 50

- Electroscope with three gold leaves, 84
- "Elementary Practical Chemistry and Qualitative Analysis" (review), 71
- "Elementary Quantitative Analysis" (review), 173
- Elements, hypothesis on the atomic motion of, 53
- periodic classification of, 31
- Elliott, W. J., action of chloroform and potash on metamidobenzoic acid, 254
- Emission of the X rays, 174
- Enamels and glasses, role of boric acid in, 305
- Endography, cranial, by the Röntgen rays, 85
- England and Germany, chemical education in, 175, 245
- Engler, C., and W. Wild, separation of ozone from hydrogen peroxide, 180
- Erchentrecher, H., determination of chlorine in bromine, 26
- Erdmann, H., ammoniacal nitrogen in primitive rocks, 64
- Eschbaum, F., oxidising properties of water distilled in copper vessels, 107
- Etaix, L., extraction apparatus, 25
- Etard, A., spectrum of the chlorophylls, 293
- Ether, 25
- and phosphoric acid in presence of water, 121
- methylic, separation of ethylic alcohol from, 110
- action of light on, 252
- pure, for narcotising, 81
- Ethereal oils and starch in adulterated cloves, micro-chemical determination of, 49
- Etherification, heat of, 37
- Ethers, chlorated, 12
- ethylic, of the chloric acetic acids, 37
- phosphopalladous and phosphopalladic, ammoniacal derivatives of, 233
- Ethyl alcohol, separation of from acetic acid, &c., 110
- oxide, adiabatic relations of, 295
- Ethylic and methylic alcohols, determination and separation of small quantities of, 110
- salts of ortho-, meta-, and para-ditolyltartaric acid, 105
- dicarboxylglutaconate, hydrolysis of, 278
- ethers of the chloric acetic acids, 37
- iodopropionate, action of on the sodium derivatives of ethylic isopropylmalonate, 119
- Ethylidenetrimethylene, 85
- Ethylxalyl, action of on naphthalene in presence of aluminium chloride, 62
- Ethylsalicidene and anisol camphors, crystallographic properties of, 49
- Euler, H., and C. Friedheim, quantitative determination of molybdenum, 38
- Evans, C. de B., tertiary benzenoid amines, 303
- Ewan, T., and H. T. Calvert, colloidal chrom-sulphuric acid, 121
- "Exercises in Practical Chemistry, mostly Quantitative" (review), 317
- Exhibitionism, 96
- "Experimental Chemistry, New Course of, including Qualitative and Quantitative Analysis" (review), 256
- Explosive, new, tetra-nitro-cellulose, 239
- Extraction apparatus, 25, 258
- Farman, sources of error in the assay of gold and silver, 318
- Farnsteiner, R., determination of sugar, 50
- Fats, analysis of, 50
- rancidification of, 197, 246
- in foods, 57
- Fatty acids, complex, thiocarbimides derived from, 290
- electrolysis of, 85
- Favra, W. W., infection of milk by bacteria, 318
- Fay, H., action of light on organic acids, 55, 67, 79
- and J. F. Norris, iodometric determination of selenious and selenic acids, 284
- Ferment of mushrooms, oxidising action of, 161
- "Ferments, Industry of" (review), 317
- Ferropyrin, 318
- Ferrous bromide, absorption of nitric oxide by, 317
- sulphate, oxidation of by seawater, 316
- Fertiliser, ground mineral phosphate as a, 4
- Filsinger, F., iodine number of cocoa butter, 236
- Filter of cellulose, 98
- pump, Geissler, as an aspirator, 230
- Finck, M., phosphopalladic and phosphopalladous ethers, ammoniacal derivatives of, 233
- Fire-damp, nitrogen and argon in, 85, 87, 97, 100
- Firefly, light of, 318
- Firth College, Sheffield, 133
- Flask, a boiling, 281
- modification of the litre, 257
- Flavizky, F., atomic motion of the elements, 53
- Fleck, H., separation of trimethylamine from ammonia, 116
- Fleischmann, W., C. M. Aikman, and R. P. Wright, "The Book of the Dairy" (review), 173
- Fléurent, E., wheat flours, 281
- Flint-glass trade, British, 193
- Flours, nutritive value of, 38
- Foods, determination of fats in, 50
- "Foods, Preserved" (review), 10
- Forensic chemistry, 110
- Formaldehyd, action of on phenylhydrazine, 120
- water upon, 73
- reactions of, 281
- volumetric determination of, 62
- Formation-heat of lithium hydride, 270
- Formic acid, determination of, 49
- evaporation heat of, 11
- Forester, M. O., base derived from camphoroxime, 1104
- Fortey, Emily C., and A. Richardson, action of light on amyl alcohol, 252
- Föth, J., yellow phosphorus, 318
- Fourlinnie, C., form of the atoms, 168
- Fractionated distillation, 25
- separation of three liquids by, 258
- Frankland, P., and F. M. Wharton, position-isomerism and optical activity, 105, 279
- Fresenius, H. H., and C. J. S. Maken, determination of phenol in soaps, &c., 197
- R. Lucium, 269
- pure starch sugar and wine obtained with its use, 26
- and E. Hintz, relations of solubility in barium sulphate, 109
- examination of thorium nitrates, and separation of ceria and thoria, 257
- W., gas analytical methods and apparatus, 109
- and P. Dobriner, sugars, 197
- L. Grünhut, examination of wines, 110, 197
- Freundler, P., chlorated ethers, 12
- fission of dioxytstearic acid, 12
- influence of solvents upon the rotative power of organic substances, 25
- Friedheim, C., and H. Euler, determination of molybdenum, 38
- Friedländer, S., argon and helium, 179
- Friewell, R. J., proximate constituents of coal, 305
- Fruit wines, distinction from grape wines, 293
- Fruits of Phoenix melanocarpa, composition of, 281
- Fungi, laccase and tyrosinase in juice of, 174
- Fusel, celluloid, 257
- analytical, 257
- hot water, 257
- Fused salts, direct spectroscopic examination of, 258
- Fusel oil, examination of fine spirit for, 109
- Fusibility of metallic alloys, 73
- Fusion- and ignition-points, 258
- GALENA, zinciferous, 114
- Gallenkamp, W., new sulphurated hydrogen apparatus, 25
- Gallic acid, reaction of, 283
- chloridation of, 49
- Galloway, W., coal-dust, 51
- Gardner, J. H., and J. E. Marsh, halogen derivatives of camphor, 279
- Garrigues, W. E., nitrogen in manures, 110
- Garrigou, F., organic matter in the mineral water of Tulba-Haut, 293
- Gas analytical methods, 109
- burners, system of, report on by M. Violle, 12
- cléveite, new elements of, 238
- flame, arrangement for automatic exhibition of, 25
- generators, 257
- in the air, 188
- "Gas and Petroleum, Incandescence by Acetylene, and its Applications" (review), 60
- "Gas and Vapour, Inflammable, in the Air, Direction and Measurement of" (review), 195
- Gases, apparatus for drying and absorbing, 257
- cock for receivers destined for compressed or liquefied, 292
- solubility of solids in, 104
- action of the electric effluve on the property of to discharge electrified bodies, 233
- "Gases of the Atmosphere, their History and their Discovery" (review), 291
- Gassmann, C., primary, secondary, and tertiary amines, 97
- Gastric liquid, examination for free hydrochloric acid in, 99
- Gautier, A., "Animal and Microbian Toxines," 37
- H., metallic alloys, 73, 84
- Geelmuyden, H. C., determination of acetone, 246
- Geissler filter-pump, as an aspirator, 230
- Gemmel, G. H., "Chemical Notes and Equations" (review), 24
- Génin and Bordes, M.M., congelation point of cows' milk, 161
- Gerard, E., fermentation of uric acid by micro-organisms, 84
- Germany and England, chemical education in, 175, 245
- Industrial accidents in, for 1895, 295
- "Germany, Made in" (review), 148
- Giles, W. M. B., modification of the litre flask, 257
- Girard, A., alimentary value of bread from flours sifted to different standards, 7, 12
- Girard, A., composition of the fruits of Phoenix melanocarpa, 281
- report on the control of agricultural distilleries, 74
- Gladding, T. S., iron oxide and alumina in phosphate rock, 112, 146
- Gladstone, J. H., and W. H. H. H., action of metals and their salts on the ordinary and the Röntgen rays—a contrast, 235
- Glasgow and West of Scotland Technical College, 135
- "Glasgow and West of Scotland Technical College, Calendar for 1896-97" (review), 108
- University, 138
- Glass cocks with a safety arrangement, 25
- Klosterneburg must, table of corrections for, 306
- alumina in the production of, 12
- stoppers, loosening, 258
- vessels for preserving substances sensitive to light, 25
- Glasses and enamels, role of boric acid in, 305
- devised by Winkelmann and Schott, mechanical and thermic properties of summarised by H. le Chatelier, 12
- Glow-worms, the emission by of rays traversing needle paper, 149
- Gluckmann, determination of volume of pulverulent bodies by shaking, 257
- Glucina, pure, properties of, 292
- Glucose, aldehyds, and ketones, reactions for, 281
- determination of, 318
- Glutaric acid, derivatives of, 253
- Glyoxylic acids of the aromatic series, action of hydrazines upon, 37
- Goats, tuberculosis in, 13
- Gold, action of silicon upon, 73
- and silver in sea-water, 146, 160, 166, 182, 191
- error in the assay of, 318
- relative weights dissolved by potassium cyanide from alloys, 106
- influence of platinum metals on assay of, 38
- in pyrites during weathering, 97
- ores and sands, assay of, 100
- separation of silver from, 2
- in sea-water, 316
- "Gold Extraction, the Cyanide Process of" (review), 195
- Goldsmiths' Institute, 137
- Gooch, F. A., and A. Kreider, alkaline perchlorates in presence of chlorides, chlorates, and nitrates, 38
- and F. S. Havens, separation of aluminum from iron, 296
- and W. C. Morgan, determination of tellurium as iodide, 189
- and A. W. Peirce, determination of selenious and selenic acids, 3
- Gouy, M., refraction and diffraction of the X rays, 61
- Granger, A., action of compounds of phosphorus upon iron, nickel, and cobalt, 84
- Grape wines, their distinction from fruit wines, 293
- "Gravitation, Speed of Propagation of the Rays of, and the Laws of their Action" (review), 149
- Green, A. G., constitution and colour, 300
- Greiner, E., glass cocks with a safety arrangement, 25
- hydrometer pipette, 109
- Grenet, L., boric acid in glasses and enamels, 306
- Griffiths, A. B., red pigment of Amanita muscaria, 11
- Grigg, G., recognition of mineral acids in acetic acid, 276
- FABRE, C., determination of potassa, 11
- Fabierz, 114

- Grosse, S., and P. Jannasch, separation of bismuth from copper and iron group, 162
- Ground rice and buckwheat, distinction between, 50
- Grünhut, L., and W. Fresenius, determination of wines, 197
- Guano, uric acid in, 229
- Guerbet, and Béhal, MM., inactive camphoric acid, 37
- Guerlain, J., and J. Dupont, essential oil of roses, 270
- Guichard, M., molybdenum iodide, 293
- "*Traité de Distillerie, Industrie de la Distillation Levures et Alcohols*" (review), 317
- Guillaume, C. E., emission of X rays, 174
- Guishard, P., analysis of yeast, 62
- Gunnell, O., and A. G. Perkin, colouring-matter of *Quercus colorado*, 120
- Guntz, M., formation-heat of lithium hydride, 270
- Gustavson, G., vinyltrimethylene and ethylenetrimethylene, 85
- HACK-FLESH**, preservation of, 49
- Hada, S., mercurous and mercuric salts, 277
- Haga, T., volumetric determination of hydroxylamine, 293
- and E. Divers, amidosulphonic acid, 277
- preparation of hydroxylamine sulphate, 269
- imidosulphonates, 269
- reduction of nitrosulphates, 269
- Hairs, Hr., detection of saccharin in presence of salicylic acid, 49
- Haller, A., and M. Minguin, camphoric mononitrate, 85
- Hallepaul, L. A., action of ammonia upon potassium or sodium paratungstates, 84
- zirconoctungstic compounds, 12
- Hallwachs, W., refractive power and density of solutions, 25
- Halogens, determination of, 49, 109, 281
- Hamonet, J., electrolysis of fatty acids, 85
- Hanamann, J., determining phosphoric acid, 38
- Hanriot, M., distribution of lipase in the organism, 291
- new ferment in the blood, 281
- Hansdorff, G., adjusting temperature in distillation, 257
- Hansek, M., and A. Lehn, distinction between ground rice and buckwheat, 50
- Hapgood, C. W., and A. A. Noyes, are diphenyliodonium and thallium nitrates isomorphous? 217
- Hart, E., "Chemistry for Beginners" (review), 208
- Hartley, W. N., argon and helium, 209
- Haselhoff, M., and C. E. Zey, nitrogen in organic substances, 293
- Have, H. M., and A. Sauveur, tempering of steel, 222
- Havens, F. S., and F. A. Gooch, separation of aluminum from iron, 295
- Heat formation of lithium hydride, 270
- of etherification, measure of, 37
- Heating by electricity, 258
- Hebert, A., isanic acid, 49
- Hefelmann, R., determination of fats in foods, 50
- zinc in American apple-rings, 49
- Heinke, J. Z., and W. H. Perkin, action of ethylic iodopropionate on the sodium derivative of ethylic isopropylmalonate, 119
- Helium and argon, 75, 85, 179, 209, 223, 260
- Henderson, G. G., and J. M. Barr, action of acidic oxides on salts of hydroxy-acids, 253
- J. B., and W. Stroud, electrolytic conductivity, 232
- J., and J. Walker, halogens in organic substances, 49
- Henriet, M., carbonic acid in the air, 64, 71
- Henry, O., utility in radiography of screens of phosphorescent zinc sulphide, the emission by glow-worms of rays traversing needle paper, 149
- E., modification of the nitrometer, 257
- L., new mixed trimethylene compounds, 97
- Herschell, G., "Cycling as a Cause of Heart Disease" (review), 305
- Herzig, J., and H. Meyer, alkyl combined with nitrogen, 49
- Hewitt, J. T., and F. G. Pope, condensation of chloral with resorcinol, 106
- and H. E. Stevenson, the three chlorobenzeneazosalicylic acids, 106
- Hexamethylenamine and some of its derivatives, 246
- Hibbert, W., and J. H. Gladstone, action of metals and their salts on ordinary and Röntgen rays, 235
- High temperatures, measurement of, 258
- Hill, R. W., loosening glass stoppers, 258
- Hillyer, H. W., aluminium alcohols, 58
- Hintz, E., and R. Fresenius, solubility of barium sulphate, 109
- commercial thorium nitrates, and separation of ceria and thorina, 257
- Hirschsohn, E., fatty oils in balsam of copaiba, 110
- Hocinchonidine and cinchonidine, distinction between, 109
- Hodgkinson, W. R., determination of fusion and ignition points, 258
- Holland, T. H., crystallography of monohydrated mercurous nitrate, 289
- Honey, examination of, 185
- "Hongkong Report of Government Analyst, 1896" (review), 149
- Hooker, S. C., constitution of lapachol and its derivatives, 152
- lomatol, 252
- Horne, W. D., apparatus for extracting soluble phosphoric acid from superphosphates, 258
- Horn, W., and J. Baumann, vacuum water-bath, 197
- Hummel, J. J., and A. G. Perkin, colouring matter in bark of *Myrica nagi*, 104
- colouring matters in various British plants, 278
- occurrence of quercetin in the onion, 56
- Humphreys, W. J., solution of metals in mercury, 289
- Hurst, G. H., "Painters' Colours, Oils, and Varnishes" (review), 47
- Hydrates, chloral and bromal, polymorphism, 95
- Hydrazines, action of upon glyoxylic acids, 27
- Hydrazones, action of formic aldehyd on some, 120
- Hydride, lithium, formation heat of, 270
- Hydrindone, derivatives of, 301
- Hydriodic and hydrobromic acids, reduction of vanadic acid by, 202
- Hydrocarbides, gaseous and liquid, formation of, 37
- Hydrochloric acid in the gastric liquid, 99
- Hydrofluoric acid, 56, 45
- Hydrogen and carbon, direct union of, 268
- apparatus, sulphuretted, 25
- compounds, action of certain, upon thionyl chloride, 306
- peroxide, detection of small quantities in organic fluids, 306
- strong solutions of, 38
- ozone from, 180
- sulphide, action of on cupric salts, 99
- thioacetic acid in place of, 73
- gas generators for, 257
- Hydrolysis of ethylic dicarboxylglutamate, 278
- Hydrometer pipette, 109
- Hydroxides and carbonates, determination of, 197
- estimation of, 116
- metallic, obtaining electrochemically, 181
- compounds of with iodine, 269
- Hydroxy-acids, salts of, action of certain acidic oxides on, 253
- Hydroxylamine sulphate, preparation of, 269
- volumetric determination of, 293
- "Hygiene, Chilean Review of" (review), 61, 280
- Hyponitrites, mercury, 289
- ICE**, production of for laboratory use, 197
- Ignition and fusion points, 258
- Ilmenite, 114
- Imidosulphonates, 269
- Impedance and admittance, 8
- Imperial Institute, scientific and technical department of, 217, 241
- "Incandescence by Gas and Petroleum, Acetylene and its Applications" (review), 60
- Indicator, luteol, a new, 25
- Indicators, coloured, and salts, neutrality of, 285
- Indoles and indol carbonic acids, recognition of, 109
- Industrial accidents in Germany for 1895, 205
- "Inflammable Gas and Vapour in the Air" (review), 195
- Insecticide, new, arsenate of lead, 17
- International catalogue conference, 58
- Iodate, potassium, in potassium iodide, 197
- Iodic acid, action of sulphuric acid and iodine upon, 293
- combinations of with other acids, 84
- Iodide method of copper assay, 52
- molybdenum, 293
- nitrogen, constitution of, 267
- potassium, detection of potassium iodate in, 197
- Iodides, alkyl, action on silver malate, 290
- and mercurous nitrite, interaction of, 289
- Iodine, action of upon stannous chloride, 49
- and bromine, replacement of chlorine by, 27
- and sulphuric acid, action of upon iodic acid, 293
- bacterial action of, 134
- compounds of metallic hydroxides with, 269
- determination of soluble compounds of, 52, 186
- alkaloids, 246
- hydroxylamine by means of, 293
- Iodine, free, gas-volumetric determination of, 109
- in water, 186
- number of cocoa butter, 109, 236
- ozoneiferous aldehyds for detection of, 7
- use of for volumetric determination of alkaloids, 24
- Iodometric determination of selenium and selenic acids, 3, 284
- of carbon dioxide, 65
- Iodoso- and iodoxy-benzaldehyds, 107
- Iridium, solubility of carbon in, 61
- Iron, action of haloid compounds of phosphorus upon, 84
- and antimony, density and specific heat of alloys of, 85
- and copper group, separation of bismuth from, 162
- oxide and alumina, in phosphate rock, determination of, 112, 146
- and other metallic oxides, dissolving, 9, 109
- in the ash of plants and animals, 306
- nickel, and cobalt, action of acetylene upon, 1
- zinc, electrolytic determination of, 9
- separation of aluminum from, 295
- wire nets with asbestos covers, 257
- "Iron, Chemical Analysis of" (review), 255
- Isanic acid, 49
- Isinglass, insoluble residue, 318
- Isobutyric aldehyd, condensation products of, 12
- Isomers of anethol, two, 62
- Isopropylglutaric acid, 107
- Isopropylmalonate, ethylic, action of ethylic iodopropionate on the sodium derivative of, 119
- JACKSON, D. H., W. R. Dunstan, and T. Tickle**, action of methyl alcohol on aconitine, 120
- Jacquemin, G., denaturation of alcohol, 37
- Jais, J., sugar in green malt, 293
- Jannasch, P., separation of mercury from arsenic, antimony, and copper, 145
- and S. Grosse, separation of bismuth from the metals of the copper and iron group, 162
- Japanese coal, 76
- tellurium, atomic weight of, 106
- Japp, F. R., and T. S. Murray, synthesis of pentacarbon rings, 105
- Jaudrier and Barbet, MM., nitrates in water, 222
- Jaworowski, A., reactions for glucose, aldehyds, and ketones, 281
- Jerdan, D. S., and W. A. Bone, union of carbon and hydrogen, 268
- John, W., and C. P. Perman, borax as standard for acids, 197
- Jolles, A., detection of urotilin, 318
- mercury in urine, 318
- Jones, F., "A Junior Course of Practical Chemistry" (review), 281
- F. W., and F. A. Willcox, analysis of cap composition, 283
- H., atomic weight of yttrium, 62
- H. C., and C. R. Allen, conductivity of solutions of acetylene in water, 18
- use of phenolphthalein in illustrating the dissociating action of water, 32
- L. C., and P. E. Browning, estimation of cadmium as the oxide, 190

Jorison, A., dulcin in beverages, 306
 Jowett, H. A. D., atisine, 120
 Jubilee of science teaching in the City of London School, 269
 "Junior Course of Practical Chemistry" (review), 281

KÄMMERER, H., preservation of hack flesh, 49
 Karlowa, A., and A. Stutzer, uric acid in guano, 229
 Kathodic rays, spectrum of, 196
 Kaufmann, H., and H. Wislicenus, aluminium amalgam, 197
 Kayser, H., progress of spectroscopy, 307
 Keiser, H., preparation of allylene, and action of magnesium upon organic compounds, 78
 Kekulé, the late Professor A. (obituary), 60
 life and work of, 291
 Keller and Maas, sulphur in roasted copper ores and cupriferos pyrites, 62
 Kelvin, I.ord, J. T. Bottomley, and M. Maclean, measurement of electric currents, 375
 "Kemp and Co.'s Prescribers' Pharmacopoeia" (review), 185
 Ketonic acids, 252
 Ketones and ketonic acids, condensation of halogen derivatives of fatty ethereal salts with, 119
 glucose, and aldehyds, reactions for, 281
 Ketopinic acid, 252
 Kern, S., cementated steels, 5
 phosphorus and sulphur in crucible steels, 76
 King's College, 125
 Kippenberger, C., quantitative isolation of alkaloids, 246
 iodine for determination of alkaloids, 24, 246
 estimation of hydroxides and carbonates, the mono- and bi-carbonates of the alkalis, alkaline earths, and magnesia, 116, 197
 Kipping, F. S., and A. Lapworth, derivatives of camphene sulphonic acids, 107, 279
 sulphocamphoric acid and derivatives of camphorsulphonic acid, 288
 and C. Revis, derivatives of hydriindone, 301
 and W. B. Edwards, dimethyl-ketohexamethylene and synthesis of dimethylhexamethenylmalonic acid, 279
 Klar, M., formaldehyd, 62
 acetone in crude acetones, 265
 Klosterneuburg must-glass, table of corrections for, 306
 Koch, F., reaction of gallic acid, tannin, pyrocatechin, and protocatechuic acid, 283
 K. R., barometer for the laboratory, 258
 Kohlrausch, F., and F. Rose, solubility of certain sparingly soluble bodies, 25
 Krämer, H., starch and ethereal oils in adulterated cloves, 49
 Kreider, D. A., and F. A. Gooch, alkaline perchlorates in chlorides, chlorates, and nitrates, 38
 and J. E. Breckenridge, separation of potassium and sodium, 227
 Krüss, G. and H., quantitative spectral analysis, 258
 Kublich, fruit wines and distinction from grape wines, 293
 Küster, F. W., volumetric determination of halogens in organic substances, 109
 Kutscheroff, M., determination of essential oils with salt, 12

LABORATORY appliances, 25
 an ideal chemical, 312
 barometer for, 258
 lays, 225
 Laborde, J., density and specific heat of alloys of iron and antimony, 85
 Laccase and tyrosinase, in the juice of fungi, 174
 Lachaud, M., capillary affinities, 11
 Lachman, A., pentaethyl nitrogen, 77
 Lander, G. D., and T. Purdie, action of alkyl iodides on silver malate, 290
 Lanthanum, atomic weight, 318
 carbide, 84
 Lapworth, A., and F. S. Kipping, derivatives of camphene sulphonic acids, 107, 279
 sulphocamphoric acid and derivatives of camphorsulphonic acid, 288
 Lapachol and its derivatives, constitution of, 252
 Lasche, determination of sugars, 110
 Lasne, H., alumina in phosphates, 369
 Lavoisier memorial, 121
 Lead, action of silicon upon, 73
 argentiferous, electrolytic disargeneration of, 37, 40
 arsenate of, 17
 chromate, analysis with, 110
 peroxide of, 144
 Lebeau, P., pure glucina, 292
 Le Chatelier, H., mechanical and thermic properties of new glasses, 12
 Lecco, Dr., iodine in water, 186
 Leduc, A., densities of nitrogen, oxygen, and argon, 292
 Lee, T. H., formaldehyd, 281
 Lefèvre's treatise on colouring matters, 74
 Léger, E., benzoyl radicle in organic substances, 276
 Leguminous plants, tubercles of, 270
 Lehn, A., and Hansek, H., distinction between ground rice and buckwheat, 50
 Leicester, J., new blue dye obtained from quinone, 236
 drying and absorbing gases, 257
 Lejeune, L., and E. Ducretet, cock for compressed gases, 292
 Lemoine, M., Röntgen rays in palaeontology, 281
 Lemout, P., researches on cyanamide, 222
 Lenher, V., and W. B. Rising, determination of mercury in cinnabar, 310
 Lescoeur, H., neutrality of salts and coloured indicators, 285
 Letts, Prof., and R. F. Blake, determining carbonic anhydride in air, 287
 Levoir, L. C., heating by electricity, 258
 Levulic acid, volatility of, 121
 Lenz, W., forensic chemistry, 110
 Lieben, A., determination of formic acid, 49
 Light, action of on amyl alcohol, 252
 on ether, 252
 on dyed colours, 205, 218
 on organic acids in presence of uranium salts, 55, 67, 79
 Lighting with acetylene, 12
 Limestone with cone-in-cone structure, 115
 Linebarger, C. E., and M. Delafontaine, reaction between carbon tetrachloride and the oxides of niobium and tantalum, 33
 Linoleum, manufacture of, 12
 Lipase in the organism, 291
 Lippmann, G., colour photography, 275, 285

Liquids, separation of three by fractionated distillation, 258
 Liquors, alcoholic, action of oxygen upon, 184
 Lister, Sir J., British Association, Liverpool, inaugural address, 139, 151
 Lithium hydride, formation heat of, 270
 as a nitrogen absorbent, 6
 dissociation spectra of salts of, 12
 Litmus, colouring power of, 297, 317
 Litre flask, modification of, 257
 Little, A., and C. Beadle, derivative of cellulose, 12
 Littleton, T., heat of formation of silver amalgam, 289
 Liversidge, A., gold and silver in sea water, 146, 160, 166, 182, 191
 New South Wales minerals, 113
 J. F., gas generators, 257
 Loemer, H., laboratory appliances, 25
 Loew, O., "The Energy of Living Protoplasm" (review), 255
 physiological action of amidosulphonic acid, 277
 Lomatol' 252
 London water supply, 41, 88, 169, 207, 243, 266, 313
 Long, J. H., inversion of sugar by salts, 203, 215, 231, 237, 249
 Longshaw, W., constitution of molecule, 199
 Lorenz, R., obtaining the metallic hydroxides electrochemically, 181
 electro-chemical production of metallic sulphides, 191
 twin elements, 217, 224
 Low, A. H., copper assay by the iodide method, 52
 Lowat, M., tempering steel with phenic acid, 317
 Lucium, a supposed new element, 159, 212, 259, 269
 Ludwig, E., ozoniferous aldehyds for the detection of iodine in presence of chlorine and bromine, 7
 Luteol, 25

MAAS and Keller, sulphur in roasted copper ores and cupriferos pyrites, 62
 Macadam, S., refuse destructors, 12
 McCrae, J., measurement of high temperatures, 197, 258
 McElroy, K. P., contraction on mixing acetone with water, 293
 and W. D. Bigelow, cane-sugar in presence of milk-sugar, 293
 McIntosh, D., conductivity of mixtures of electrolytes, 21, 35, 44
 MacLagan, T. J., "Rheumatism, its Nature, its Pathology" (review), 24
 MacLaurin, J. S., gold and silver dissolved by potassium cyanide, 106
 Maclean, M., Lord Kelvin, and J. I. Bottomley, measurement of electric currents, 175
 McLeod, H., liberation of chlorine from potassic chlorate and manganic peroxide, 95
 Maesse, R., determination of high temperatures, 150
 Magalhães, A. J. de Cruz, caramel in wines, 306
 Magenta, distinctive character of ordinary and of acid magenta S, 117
 Magnesia, mono- and bi-carbonates of, 116, 197
 Magnesium chromite, 306
 cobaltite, 85
 phosphate calculating the phosphoric acid in, 110
 action of upon organic compounds, 78

Maken, C. J. S., and H. H. Freisenius, phenol in soaps and disinfective preparations, 197
 Malaria, influence of trees on, 48
 Malate, silver, action of alkyl iodides on, 290
 Malt, green, sugar in, 293
 Maltézos, C., X rays, 37
 Manganese in steel, 214, 248, 262
 peroxide and potassic chlorate, liberation of chlorine from, 95
 Manures, nitroferous, nitrogen in, 110
 Manurial matter containing phosphoric acid, 318
 salts, potassa in, 318
 Marne, the Seine, and the Yonne, nitric acid in the waters of, 305
 Marsh, J. E., and J. H. Gardner, researches on the terpenes, 279
 Marshall, B. M. C., rotation of aspartic acid, 105
 Miss D., evaporation heat of formic acid, 11
 Mascart, M., scientific explorations in balloons, 305, 317
 Mason, W. J., chemical analysis and bacteriological examination of potable water, 73
 Matignon, C., and M. Deligny, nitro-substitutions, 12
 Maul, R., and A. Stutzer, examination of spirit for fusel oil, 109
 Maxima of spectra, periodic, 246
 Mayer, A. M., Röntgen rays, 7, 19
 Mechanics and Biological Chemistry, 67
 "Medical Guide, Everybody's" (review), 208
 Meillière, G., chlorine in organic products, 109
 Meinecke, C., potassium biniodate, 197
 Meldola, R., G. H. Woolcott, and E. Wray, chemistry of phenol derivatives, 251
 Meldrum, R., bacterial action of potassium permanganate, chromic acid, and iodine, 184
 Melted salts, dissociation spectra of, 12
 Melting-point and critical temperature, relation between, 101
 Melting-points of some inorganic salts, 197, 258
 Mercurial air-pumps, 25
 Mercuric and mercurous salts, 277
 Mercurous nitrite and the alkyl iodides, interaction of, 289
 monohydrated, crystallography of, 289
 Mercury, hyponitrites, 289
 in cinnabar, 310
 in urine, 318
 nitrites of, 289
 solution and diffusion of metals in, 289
 oxy-salts of, 84
 salts, action of on aluminium, 30
 separation of from arsenic, antimony, and copper, 145
 poisoning, 40
 Merritt, H., assay of gold ores and sands, 100
 Messenger's method for determination of acetone, 246
 Metallic alloys, 84
 fusibility of, 73
 carbides, 15, 37
 chlorides, action of phosphorus on, 37
 hydroxides, obtaining electrochemically, 181
 compounds or with iodine, 269
 sulphides, electro-chemical product on of, 191
 tubes and discs, action of upon the X rays, 73
 Metallurgical products, spectrum of phosphorus in, 41, 49
 Metals and alloys, solution and diffusion of in mercury, 289

- Metals and their salts, action of on the ordinary and on the Röntgen rays, 235, 257
 evaporation of at the ordinary temperature, 72
 of the copper and iron group, separation of bismuth from, 162
 structure of, 174
 volumetric determination of, 109
 "Metals, Tabular Atlas of Chemistry of" (review), 185
 Metamidobenzoic acid, action of chloroform and potash on, 254
 Meta-, ortho-, and para-ditoluyl-tartaric acid, methylic and ethylic salts of, 105
 Meter, a consistency, 258
 Methyl acetate, separation of ethylic alcohol from, 110
 alcohol, action of on aconitine, 120
 and ethylsalicylenes and anisole camphors, crystallographic properties of, 49
 benzaconine, formation of, 120
 heptenone, natural, 12
 nitrate, 12
 Methylic and ethylic alcohols, determination and separation of, 110
 salts of ortho-, meta-, and para-ditoluyltartaric acid, 105
 ether, separation of ethylic alcohol from, 110
 Metzner, R., preparation of selenic acid, 85
 Mewes, R., "Die Fortpflanzungs-Geschwindigkeit der Schwerkraftsstrahlen und deren Wirkungsgesetze" (review), 149
 Meyer, F., bottle with liquid joint, 25
 H., and J. Herzog, alkyl combined with nitrogen, 49
 V., and T. S. Patterson, iodoso- and iodoxy-benzaldehyds, 107
 Microbial and animal toxins, 37
 Micro-organisms, fermentation of uric acid by, 84
 Mietzschke, W., gold in pyrites, 318
 Milk, congelation point of, 161
 examination of, 50
 infection of by bacteria, 318
 Milk-sugar, commercial, ash in, 50
 cane-sugar in presence of, 293
 determination of, 49
 Mineral acids in presence of organic acids, 49
 in presence of acetic acid, 276
 oils, vegetable and animal oils in, 62
 phosphate, ground, as a fertilizer, 4
 water of Tulba-Haut, organic matter in, 293
 Minerals, direct spectroscopic examination of, 258
 Minguin, J., crystallographic properties of benzylidene, methyl- and ethylsalicylenes, and anisole camphors, 49
 crystallographic properties of some alcyoncamphors of the aromatic series, 85
 and A. Haller, camphoric mononitrite, its anhydride and its anilide, 85
 Moissan, H., preparation of the diamond, 85
 formation of gaseous and liquid hydrocarbons by the action of water upon the metallic carbides, 37
 preparing alloys, 11
 metallic carbides, 15
 tungsten, 61
 solubility of carbon in rhodium, iridium, and palladium, 61
 lanthanum carbide, 84
 diamantiferous sands of Brazil, 97
 Moissan, H., the black diamond, 85
 cast vanadium and vanadium carbide, 11, 29
 and C. Mouret, action of acetylene upon iron, nickel, and cobalt, 1
 Molecule, constitution of, 199
 Molybdate solution, ammonium, 35
 Molybdenite, 115
 Molybdenum, atomic weight of, 62
 determination of, 38
 iodide, 293
 Monazite, Brazilian and Carolina, 74
 constituents of, 274
 sands, earths of the yttria group contained in, 292
 Mond, L., address to the chemical section of the British Association, Liverpool, 156, 163
 Monochloric acetal, 37
 Mononitrite, camphoric, its anhydride and its anilide, 85
 Moor, C. G., and T. H. Pearmain, "Applied Bacteriology" (review), 207
 Morgan, J. J., sulphur in cast iron or steel, 257
 W. C., and F. A. Gooch, determination of tellurium, 189
 Möhrner, K. A. H., reaction for acetaetic acid in urine, 318
 Morphotropic relations of naphthol derivatives, 302
 Mouret, C., and H. Moissan, action of acetylene upon iron, nickel, and cobalt, 1
 Mouret, C., isomers of anethol, 62
 Mourlot, A., action of high temperatures on sulphides, 62
 Moussard, E., photographing objects in relief and depression, 72
 Muencke, R., an analytical funnel, 257
 Muntz metal sheathing, removal of silver and gold from seawater by, 182, 191
 Muraoko, light rays of the firefly, 318
 Murray, T. S., and F. R. Japp, pentacarbon rings, 105
 Muscles, chemical process which governs the transformation of the potential, 11
 Mushroom, analysis of air by, 247, 292
 Mushrooms, ferment of, action of upon phenols, 161
 Musical tubes, 304
 Must glass, Klosterneuburg, table of corrections for, 306
 Myrica nagi, colouring matter in, 104
 NAG, N. C., salts of cobalt and nickel, 212
 Naphthalene, action of ethyloxalyl on, 62
 "Naphthalin, Derivatives of which possess Technical Interest" (review), 72
 Naphthol derivatives, morphotropic relations of, 302
 Naphtholic sulpho-acid, 293
 Naphthols and naphthylamines, behaviour of with nascent bromine, 109
 Naphthylaminic sulpho-acid, 293
 Naudin, C., tubercles of leguminous plants, 270
 Neitzel, colorimetric determination of carbohydrates, 293
 detection of sugar, 293
 Nessler, J., Spanish earth for clarifying wines, 306
 Nets, iron wire, with asbestos covers, 257
 Newth, G. S., experiments with ozone, 95
 "Chemical Lecture Experiments" (review), 256
 Nicholson, H. H., and S. Avery, electrolytic determination of iron, nickel, and zinc, 91
 Nickel, action of haloid compounds of phosphorus upon, 84
 and cobalt, new salts of, 212
 dioxide, barium dinickelate, existence and acid properties of, 196
 distinction between articles of silver and of, 318
 iron, and cobalt, action of acetylene upon, 1
 and zinc, electrolytic determination of, 91
 in steel, &c., 16
 Nicotin and ammonia in tobacco, 185
 Niebel, examination of caviare, 49
 Niobium and tantalum, oxides of, reaction between carbon tetrachloride and, 33
 Nickel, mineral acids in presence of organic acids, 49
 Nitrates, reduction of, in plants, 37
 detection of alkaline perchlorates in presence of, 38
 Nitrate, commercial thorium, 257
 Nitration, notes on, 301
 Nitric acid in the waters of the Seine, the Yonne, and the Marne, 305
 nitrogen in presence of organic nitrogen, 110
 oxide, absorption of by ferrous bromide, 317
 Nitroferous manures, nitrogen in, 110
 Nitrite, mercurous, and the alkyl iodides, the interaction of, 289
 monohydrated mercurous, crystallography of, the 289
 Nitrites in water, 222
 of mercury, 289
 recognition of, the 6
 in the air, 230, 240
 Nitrosodisulphonic acid, blue, and its salts, 97
 "Nitro-explosives" (review), 23
 Nitrogen, 38, 292
 absorbent, 6
 ammoniacal, in primitive rocks, 64
 and argon of firedamp, 85, 87, 97, 100
 atmospheric, fixation of, by algae and bacteria, 293
 alkyl combined with, 49
 in arable soils, 110
 in nitroferous manures, 110
 in organic substances, 293
 iodide, constitution of, 267
 pentaethyl, 77
 peroxide, action of upon antimony tetrachloride, 61
 Nitrogenous organic bodies, behaviour with potassium polysulphides, 186
 Nitrometer, modification of the, 257
 Nitro-naphthols, derivatives of, 302
 Nitroso-compounds of osmium, action of reducing agents upon, 84
 Nitrosodisulphonic acid, deep blue, 34, 49
 Nitro-substitutions, 12
 Nitrosulphates, reduction of, 269
 "Non-metallic Elements, Chemical Lecture Experiments" (review), 256
 Nordlinger, H., examination of water, 50
 Norman, R., and E. Täuber, "Die Derivate des Naphthalins" (review), 72
 Norris, J. F., and H. Fay, determination of selenious and selenic acids, 284
 "North Wales, University College of, Calendar for 1896-7" (review), 256
 Noyes, A. A., and C. W. Hapgood, are diphenyliodonium and thallium nitrates isomorphous? 217
 Nut, areca, poisoning by, 295
 OBITUARY, the late Professor Kekulé, 60
 Oesterle, O., and A. Techirich, colour reactions of saffron and its adulterants, 306
 Offermann, sulphocyanogen in ammonium sulphate, 317
 Oil of bergamot, 25, 246
 fusel, examination of spirit for, 109
 of reseda root, 74
 resin, essential, 281
 roses, French essential, 270
 Oils, analysis of, 50
 determination of the essential, 12
 ethereal, and starch in adulterated cloves, 49
 fatty, in balsam of copaiva, 110
 mineral, vegetable and animal oils in, 62
 Olive oil, crude, examination of, 74
 Onion, occurrence of quercetin in, 96
 Ores, sulphur in, 189, 224
 roasted copper, sulphur in, 62
 "Organic Analysis, Commercial" (review), 108
 matter in the mineral water of Tulba-Haut, 293
 of the soil, oxidation of, 97
 salts, zinc in, 186
 Ortho-, meta-, and para-ditoluyl-tartaric acid, the methylic and ethylic salts of, 105
 Osmium, nitroso-compounds of, 84
 Osmond, F., and Prof. Roberts-Austen, structure of metals, its genesis, and its transformations, 174
 O'Sullivan, C., and A. L. Stern, dextrose from different sources, 289
 Oxide, carbonic, in the air, 188
 ethyl, adiabatic relations of, 295
 ignited iron, and other metallic oxides, process for dissolving, 9, 103
 nitric, absorption of by ferrous bromide, 317
 Oxybenzoic acids and their derivatives, combination of antipyrine with, 11
 Oxygen, action of upon alcoholic liquors, 184
 densities of, 292
 determination of, 199
 explosion of acetylene with, 268
 Oxy-iodide, bismuth, 200
 Oxy-salts of mercury, 84
 Ozone, experiments with, 95
 separation of, from hydrogen peroxide, 180
 Ozoniferous aldehyds for the detection of iodine, 7
 Ozoniser, report on G. Segay's, 74
 "PAINTERS' Colours, Oils, and Varnishes" (review), 47
 Palæontology, Röntgen rays in, 281
 Palladium, solubility of carbon in, 61
 Paraditoluyltartaric acid, methylic and ethylic salts of, 105
 "Parallelogram of Forces, as Foundation of the Periodic System in Chemistry" (review), 11
 Paratungstates, potassium or sodium, action of ammonia upon, 84
 Paris Observatory Directorship, 284

- Park, J., "Cyanide Process of Gold Extraction" (review), 195
- Patein, G., and E. Dufau, combination of antipyrine with the oxybenzoic acids and their derivatives, 11
- Patterson, T. S., and Victor Meyer, iodoso- and iodoxybenzaldehydes, 107
- Payne, G. F., cotton seeds, 196
- Pearmain, T. H., and C. G. Moor, "Applied Bacteriology" (review), 207
- Peirce, A. W., selenium monoxide, 200
- and F. A. Gooch, determination of selenious and selenic acids, 3
- gravimetric determination of selenium, 66
- Pellat, H., evaporation of metals at the ordinary temperature, 72
- Pentacarbon rings, 105
- Pentaethyl nitrogen, 77
- Pentaerythrite, action of sulphur chloride upon, 84
- Penumbra, illusions which accompany the formation of, 505
- Perchlorates, alkaline, in presence of chlorides, chlorates, and nitrates, 38
- Perdrix, L., action of permanganate on the polyatomic alcohols, 317
- Periodic Law, 278
- maxima of spectra, 246
- "Periodic Law, Development of the" (review), 221
- "Periodic System in Chemistry" (review), 11
- Perkin, A. G., acid compounds of natural yellow colouring matters, 252
- and G. Allen, colouring matter of Sicilian sumach, 120
- and J. J. Hummel, quercetin in the onion, 96
- colouring matter in Myrica nagi, 104
- colouring matters occurring in various British plants, 278
- and O. Gunnell, colouring matter of Quercus colorado, 120
- Perkin, W. H., isopropylglutaric acid, 107
- derivatives of propionic acid, of acrylic acid, and of glutaric acid, 253
- acid, camphorophylic acid, camphoric acid, and camphoronic acid, 285
- and J. F. Thorpe, condensation of halogen derivatives of fatty etheral salts with ketones and ketonic acids, 119
- and J. Z. Heinke, action of ethylic iodopropionate on the sodium derivative of ethylic isopropylmalonate, 119
- and W. H. Bentley, acetobutyric acid, 253
- Perman, E. P., and W. John, borax as a standard for acids, 197
- W. Ramsay, and J. Rose-Innes, adiabatic relations of ethyl oxide, 295
- Permanganate, action of on the polyatomic alcohol, 317
- bacterial action of, 184
- standardising, 191, 246
- Perrin, J., discharges of the Röntgen rays; influence of pressure and temperature, 305
- part played by the dielectric in the discharge of Röntgen rays, 121
- Peru, balsam of, 110
- Peska, Zdenek, determination of sugar, 50
- "Petroleum and Gas, incandescence by, Acetylene and its applications" (review), 60
- Pfeiffer, T., and H. Thurmman, nitric nitrogen in presence of organic nitrogen, 110
- H., table of corrections for the Klosterneuburg must glass, 306
- Phagocytosis, excitement of, 196
- "Pharmacopœia, Prescribers'" (review), 185
- Phelps, I. K., determination of carbon dioxide, 65
- Phenic acid, tempering steel with, 317
- Phenol derivatives, chemistry of, 251
- in soaps and disinfective preparations, 197
- Phenolphthalein, use of in illustrating the dissociating action of water, 32
- Phenols, action of ferment of mushrooms upon, 161
- separation of ethylic alcohol from, 110
- enylhydrazine, action of formic aldehyde on, 120
- Philip Harris and Co., "Catalogue of Chemical Apparatus and Chemicals" (review), 148
- Phillips, H. J., substitute for the chemical balance, 257
- Phipson, T. L., analysis of air by a mushroom, 247, 292
- thermometers, 75
- explanation of the Röntgen rays, 260
- Phisalix, C., action of the porcelain filter upon the poison of the viper, 12
- Phoenix melanocarpa, fruits of, 281
- Phosphate, magnesium, table for calculating the phosphoric acid in, 110
- rock, determination of iron oxide and alumina in, 112, 146
- Phosphates, determination of alumina in, 309
- Phosphopalladic ethers, ammoniacal derivatives of, 233
- Phosphorescent zinc sulphide, 149
- Phosphoric acid and ether, reactions between, 121
- determining by means of molybdenic solution, 38
- determination of, 45
- researches on, 292
- soluble, extracting from superphosphates, 258
- table for calculating in magnesium phosphate, 110
- valuation of manurial matter containing, 318
- Phosphorus, action of haloid compounds of upon iron, nickel, and cobalt, 84
- on metallic chlorides, 37
- and sulphur in crucible steels, 76
- spectrum of, in fused salts, 41, 49
- yellow, 318
- Photographic plate, action of zinc upon, 61
- shutter, efficiency of, 280
- Photographing objects in relief and depression, process for, 72
- Photography, colour, 275, 285
- "Photography, Beginners' Guide to" (review), 72
- Physical Society, 8, 232, 254, 280, 304
- Physics, applications of to seismology, 304
- Physiological action of amido-sulphonic acid, 277
- Pichard, P., reactions of brucine, detection of nitrous nitrogen in presence of sulphites, 240
- Pictet, R., critical points of liquids as a criterion of their purity, 25
- Pinacolone, constitution of, 85
- Pinene tetrabromide, products from, 94
- action of bromine on, 94
- Pipettes, 109, 257, 258
- Plants, leguminous, tubercles of, 270
- and animals, iron in the ash of, 306
- British, colouring-matters occurring in, 278
- reduction of nitrates by, 37
- alumina in the ash of, 306
- Platinum, action of silicon upon, 73
- determination of, 38
- Poisoning by areca nut, 295
- mercury in cases of, 40
- Pollard, W., and K. Seubert, atomic weight of molybdenum, 62
- Pollock, Mr., and Prof. Threlfall, Röntgen's rays, 254
- Polysulphides, potassium, behaviour of nitrogenous organic bodies with, 185
- Ponsot, A., congelation-point of dilute aqueous solutions, 85
- Pope, F. G., and J. T. Hewitt, condensation of chloral with resorcinol, 106
- W. J., camphoric acid and acetone, 283
- chloral and bromal hydrates, 95
- refraction constants of crystalline salts, 268
- Position-isomerism and optical activity, 105, 279
- Potable water, chemical and bacteriological examination of, 73
- Potash and chloroform, action of on metamidobenzoic acid, 254
- Potassa, determination of, 11
- in manurial salts, 313
- Potassium and other bases, reproduction of double silicates of, 270
- and sodium, separation, 227
- binodate, 197
- determination of, 38
- iodate in potassium iodide, 197
- non-refraction of the X rays by, 97
- or sodium paratungstates, action of ammonia upon, 84
- polysulphides, behaviour of nitrogenous organic bodies with, 186
- sodium, lithium, alkaline metals, dissociation spectra of melted salts, 12
- tintride, separation of thorium from the other rare earths by means of, 314
- Potatoes, starch in, 306
- Pottevin, H., filter of cellulose, 98
- "Practical Chemistry, a Guide to" (review), 209
- "Practical Chemistry, Exercises in, mostly Quantitative" (review), 317
- "Prescribers' Pharmacopœia" (review), 185
- Propionic acid, some derivatives of, 253
- Proteid substances in beer wort, 185
- Protocatechuic acid, reaction of, 283
- "Protoplasm, Living, the Energy of" (review), 255
- Froustite, 115
- Prunier, L., methylic and ethylic alcohols, 110
- Pulverulent bodies, determination of volume of by shaking, 257
- Purdie, T., and G. D. Lander, action of alkyl iodides on silver malate, 290
- Pyrazolone derivatives, formation of from chlorofumaric acid, 252
- Pyrites, cupriferos, sulphur in, 62
- Pyrocatechin, reaction of, 283
- Pyrogallol, alkaline, determination of oxygen by, 199
- Pyrophosphoric acid, determination of, 292
- transformation of, 292
- "QUALITATIVE Analysis, Elementary Practical Chemistry and" (review), 71
- "Qualitative and Quantitative Analysis, A New Course of Experimental Chemistry; including the Principles of" (review), 256
- "Quantitative Analysis, Inorganic, Select Methods in" (review), 317
- "Quantitative Chemical Analysis, Elementary" (review), 173
- Quercus colorado, colouring-matter of, 120
- Quercetin, occurrence of in onion, 96
- Quinine, blue dye obtained from, 236
- RAIKOW, P. N., automatic exhibition of a gas flame after a given time, 25
- Ramsay, W., and J. N. Collie, homogeneity of argon and of helium, 75, 85, 299
- an ideal chemical laboratory, 312
- J. Rose-Innes, and E. P. Perman, adiabatic relations of ethyl oxide, 295
- "The Gases of the Atmosphere, their History and their Discovery" (review), 291
- Ray, P. C., interaction of mercurous nitrite and the alkyl iodides, 289
- mercury hyponitrites, 289
- nitrites of mercury, conditions under which they are formed, 289
- Rayleigh, Lord, argon and helium, 260
- Rays, uranic, various properties of, 305
- kathodic, spectrum of, 196
- ordinary and Röntgen, action of metals and their salts on, 235
- "Rays of Gravitation, the Speed of Propagation of, and the Laws of their Action" (review), 149
- Refraction constants of crystalline salts, 268
- Refrigerator for distillations from a test-glass, 257
- Refuse destructors, 12
- Reid, W. F., manufacture of linoleum, 12
- Remy, C., and G. Contremoulin, cranial endography by the Röntgen rays, 85
- use of X rays for anatomic research, 270, 295
- Reseda root, oil of, 74
- Resin, essential oil of, 281
- Resorcin, detection of tartaric acid by means of, 276
- Resorcinol, condensation of chloral with, 106
- Rettie, T., compounds of metallic hydroxides with iodine, 269
- Revis, C., and F. S. Kipping, derivatives of hydrindone, 301
- Revolver pipette, 258
- Reynolds, O., dryness of saturated steam, 235
- "Rheumatism, its Nature, its Pathology, and its Successful Treatment" (review), 24
- Rhodium, solubility of carbon in, 61
- Rhus coriaria, Sicilian sumach, the colouring-matter of, 120
- Richards, Dr. J. W., separation of silver from gold by volatilisation, 2
- P. A. E., action of mercury salts on aluminium, 30
- "A Guide to Practical Chemistry for the Conjoint Board" (review), 209
- Richardson, A., detection of hydrogen peroxide in organic fluids, 306

- Richardson, A., and Emily C. Fortey, action of light on ether, 252
on amyl alcohol, 252
- Reiger, E., soluble compounds of iodine, 52, 186
determination of uric acid, 25
optical determination of alcohol and extract in wines, 25
valuation and standardising of solutions of permanganate, 191, 246
- Righi, A., electric convection following the lines of force produced by Röntgen's rays, 149
- Ripper, M., iron in the ash of plants and animals, 306
- Rising, W. B., and V. Lenher, mercury in cinnamon, 310
- Rivals, P., acetal and monochloric acetal, 37
ethylic ethers of the chloric acetic acids, 37
solutions of trichloroacetic acid, 85
- Roasted copper ores and cupriferos pyrites, sulphur in, 62
- Roberts-Austen, Prof., and F. Osmond, structure of metals, 174
solution and diffusion of metals in mercury, 289
- Rochebelle gas, nitrogen and argon in, 87, 97
- Rock, phosphate, iron oxide and alumina in, 112, 146
- Rocks, ammoniacal nitrogen in primitive, 64
- Röntgen rays, 7, 19, 39, 121, 254, 260, 270
action of upon the bacillus of diphtheria, 73
metals and their salts on the ordinary and on the, 235, 257
cranial endography by means of, 85
discharge of, influence of pressure and temperature, 305
in palaeontology, 281
permeability of various elements to the, 298
electric convection following the lines of force produced by, 149
part played by the dielectric in the discharge of, 121
- Roscoe, Sir H., chemical education in England and Germany, 175
- Rose, F., and F. Kohlrausch, solubility of bodies from the electric conductivity of their solutions, 25
- Rose-Innes, J., E. P. Perman, and W. Ramsay, adiabatic relations of ethyl oxide, 295
- Roses, French essential oil of, 270
- Rossel, M., steel diamonds, 73
- Rossing A., blackening of preserved vegetables, 25
- Rousset, L., action of ethyloxalyl on naphthalene in presence of aluminium chloride, 62
- Royal Institution, 57, 234, 293
School of Mines and Royal College of Science, 126
Society, 282
Technical High School at Aachen, programme, 159
Rudd, R. T., musical tubes, 304
- Ruhemann, S., and C. G. L. Wolf, ketonic acids, 252
formation of pyrazolone derivatives, from chlorofumaric acid, 252
- Ruos, Dr., determination of the metals precipitable by fixed alkalis, 109
- Rydberg, J. R., new elements of clèveite gas, 238
- SABATIER, P., cuprous compounds for the recognition of the nitrites, 6
blue nitrosodisulphonic acid, 49, 97
- Sabatier, P., deep blue nitrosodisulphonic acid, 34
- Saccharin in presence of salicylic acid, 49, 306
- Saffron and its adulterants, colour reactions of, 306
- Sagnac, G., formation of penumbrae, 305
- Sakurai, J., molecular conductivity of amidosulphonic acid, 277
- Salicylic acid, saccharin in presence of, 49, 306
- Salts and coloured indicators, 285
crystalline, refraction constants of, 268
inorganic, measurement of the melting points of some, 197, 258
melted, dissociation-spectra of alkaline metals—sodium, potassium, lithium, 12
volatilisation of during evaporation of water, 258
- Sanford, P. G., "Nitro-Explosives" (review), 23
- Santalal and some of its derivatives, 95
- Sauveur, A., and H. M. Have, tempering of steel, 222
- Schade, O., balsam of Peru, 110
- Schar, E., reactions of acetanilide, 62
- Scheelite, 115
- Scheiding, F., sources of error in alkalimetry, 172, 197
- Schierholz, C., determination of the halogens, 109
- Schiff and Tarugi, MM., thioacetic acid in analysis, 73
- Schloiff, P., solutions of hydrogen peroxide, 38
- Schjerning, H., proteid substances present in beer wort, 185
- Schlossing, T., nitric acid in the waters of the Seine, the Yonne, and the Marne, 305
nitrogen and argon in fire-damp and in the Rochebelle gas, 85, 87, 97, 100
uniformity of the distribution of argon, 270
- Schneider, A., valuation of crude cresol, 62
- Schott and Winkelmann, properties of certain new glasses devised by, 12
- Schützenberger, P., report on G. Segny's ozoniser, 74
atomic weights of cerium, didymium, and lanthanum, 318
and M. Boudouard, earths of the yttria group contained in monazite sands, 292
- Science and Art Department, 174, 185, 196
questionable application of, 150
teaching in the City of London School, jubilee of, 217, 269
- Scientific Department of the Imperial Institute, 217, 241
explorations in balloons, 305, 317
- Sea-water, gold and silver in, 146, 160, 166, 316
oxidation of ferrous sulphate by, 316
- Sedleky and A. Belashoubek, thalleioquin reaction, 100
- Seeds, cotton, 196, 221, 281
- Segny's G., ozoniser, report by M. Schützenberger, 74
- Seine, the Yonne, and the Marne, nitric acid in the waters of, 305
- Seismology, applications of physics and mathematics to, 304
- Selenium monoxide, 200
"Select Methods in Inorganic Quantitative Analysis" (review), 317
- Selenic acid, 85
and selenious acids, iodometric determination of, 3, 284
- Selenium, determination of, 66
- Sell, W. J., citrazinic acid, 253
- Seubert, K., and W. Pollard, atomic weight of molybdenum, 62
- Sheffield Borough Analysts' Laboratory, 138
- Shimer, P. W., silica in blast-furnace slags, 318
- Shutt, F. T., arsenate of lead, 17
ground mineral phosphate as a fertiliser, 4
- Sicilian sumach, colouring-matter of, 120
- Silica, in blast-furnace slags, 318
- Silicates, double, of potassium and other bases, 270
- Silicide of calcium, 33
- Silicon, action of upon the alkaline metals, zinc, aluminium, lead, tin, antimony, bismuth, gold, and platinum, 73
- Silk, absorption of dilute acids by, 105
- Silver amalgam, heat of formation of, 289
and gold in sea-water, 146, 160, 166
assay of, 2, 318
relative weights of, dissolved by potassium cyanide, 105
removal of from sea-water by Muntz metal sheathing, 182, 191
distinction between articles of, and of nickel, 318
haloids, solubilities of in organic and inorganic solvents, 109
malate, action of alkyl iodides on, 290
oxidation of, 310
separation of from gold by volatilisation, 2
- Sinai, copper mines of, 121
- Sjögquist, J., free hydrochloric acid in the gastric liquid, 99
- Skinner, F. F., prevention of corrosive liquids being drawn into the mouth when filling pipettes, 257
- Slags, silica in blast furnace, 318
- Sleeper, J. F., "A Tabular Atlas of the Chemistry of the Metals" (review), 185
- Smale, F. J., solution of uric acid in urine, 318
- Smeetham, A., cotton seeds, 221
- Smith, C., and C. F. Cross, carbohydrates of cereal straws, 177
and E. J. Bevan, carbohydrates of barley straw, 267
- E. A., cupellation of bismuth-silver alloys, 318
- F. C., and B. W. Cheever, "Select Methods in Inorganic Quantitative Analysis" (review), 317
- H. M., boiling flask, 281
- Snap, H. L., replacement of chlorine by bromine and iodine, 27
- Soaps and disinfective preparations, phenol in, 157
- Society, Chemical, 94, 104, 119, 251, 266, 277, 286, 300, 316
of Arts, 13, 257, 245, 315
Physical, 8, 234, 289, 304
Royal, 282
- Sodic alcohol, 37
- Sodium derivative of ethylic isopropylmalonate, action of ethylic iodopropionate on, 119
potassium, lithium, alkaline metals, dissociation-spectra of melted salts, 12
and potassium, separation of, 227
or potassium paratungstates, action of ammonia upon, 84
sulphide, and hydrosulphide, oxidation of by electrolysis, 70, 80
solubility of bismuth sulphide in, 169
- Sohniewindt, iron-wire nets with asbestos covers, 257
- Soil, oxidation of the organic matter of, 97
- Soils, nitrogen in arable, 110
Solids, solubility of in gases, 194
Solubility, curves of, 233
- Sonstadt, E., oxidation of ferrous sulphate by sea-water, and on the detection of gold in sea-water, 316
- South London School of Pharmacy, 137
West London Polytechnic, 137, 150
- Spaeth, E., rancidification of fats, 197, 246
- Spanish earth for clarifying wines, 306
- Spectra of non-metals in melted salts, 11
periodic maxima of, 246
- Spectral analysis, quantitative, 258
- Spectroscopes, construction of the slit of, 258
- Spectroscopic examination of minerals and of some fused salts, 258
- Spectroscopy, bibliography of, 222
progress of, 307
- Spectrum of phosphorus in fused salts, 41, 49
the chlorophylls, 293
kathodic rays, 196
ultra-violet, absorption of by crystalline substances, 199, 204
- Spencer, A. E., and L. M. Dennis, zirconium tetraiodide, 102
- Sperber, J., "Das Parallelogramm der Kräfte als Grundlage des Periodischen Systems in der Chemie" (review), 11
- Spica, potassium iodate in potassium iodide, 197
- Spirit, examination of for fusel oil, 109
- Spring, W., colour of alcohols, 181
- Stahl, Carl F., hydrofluoric acid, 39, 45
- Stannous chloride, action of iodide upon, 49
- Stansbie, J. H., estimation of sulphur in ores, 189
- Starch and ethereal oils in adulterated cloves, 49
in cereals, potatoes, and commercial starches, 306
sugar, on technically pure, and on wine obtained with its use, 26
- Starches, commercial, starch in, 306
- Steel, tempering of, 222
diamonds, 73
manganese in, sources of error in determining, 214, 248, 262
or cast-iron, sulphur in, 76, 257
tempering, with phenic acid, 317
&c., nickel in, 16
- Steels, crucible, phosphorus and sulphur in, 76
cemented, 5
- Stern, A. L., and C. O'Sullivan, identity of dextrose from different sources, 289
- Stevenson, H. E., and J. T. Hewitt, the three chlorobenzeneazosalicylic acids, 106
- Stickney, Delia, reduction of copper sulphide, 18
- Stillman, T. B., solubility of bismuth sulphide in sodium sulphide, 169
- Stirrer, an auto-pneumatic, 63
- Stockport Technical School, 138
- Straws, cereal, carbohydrates of, 177
- Strohl, A., iodine number and the index of refraction of cacao butter, 109
- Stroud, W., and J. B. Henderson, measuring electrolytic conductivity, 232
- Students, address to, 123
- Stutzer, A., and A. Karlowa, uric acid in guano, 229

- Stutzer, A., and R. Maul. examination of spirit for fusel oil, 109
revolver pipette, 258
chemical examination of cheese, 257
- Sugar, 50, 110, 197, 276, 293
inversion of by salts, No. II., 203, 215, 231, 237, 249
- Sugars, decomposition of under the influence of acids, 233
- Sulphate, barium, solubility in, 109
ferrous, the oxidation of by sea-water, 316
- Sulphide, sodium, solubility of bismuth sulphide in, 169
hydrogen, action of on cupric salt solutions, 99
- Sulphides, metallic, electro-chemical production of, 191
- Sulphites, nitrous nitrogen in presence of, 233, 240
- Sulpho-acids, naphtholic and naphthylaminic, 293
- Sulphocamphoric acid and derivatives of camphorsulphonic acid, 288
- Sulphocamphylic acid, camphoric acid, and camphoronic acid, 286
- Sulphocyanogen in technical ammonium sulphate, 317
- Sulphur and phosphorus in crucible steels, 76
chloride, action of upon penterythrite, 84
in cast-iron or steel, 76, 257
in ores, 189, 224
in pyrites, 62
in roasted copper ores and cupriferrous pyrites, 62
specific heat of in the state of viscosity, 97
- Sulphuretted hydrogen apparatus, 25
gas generators for, 257
- Sulphuric acid, 187, 246
and iodine, action of upon iodic acid, 293
and sulphurous acids in the combustion of coal-gas, 24
- Sumach, Sicilian, *Rhus coriaria*, colouring matter of, 120
- Surgeon's Hall, Edinburgh, 138
- Sutherland, J., manufacture of alumina, 222
- Sutton, F., "A Systematic Handbook of Volumetric Analysis" (review), 173
- Synthesis of dimethylhexamethenylmalonic acid, 279
- "Systematic Handbook of Volumetric Analysis" (review), 173
- TANNIN**, reaction of, 283
- Tanning materials, examination of, 306
- Tantalum and niobium, oxides of reaction between carbon tetrachloride and, 33
- Tartaric acid and its alkaline salts, 281
detection of by means of resorcin, 276
- Tarugi and Schiff, MM., use of thioacetic acid in analysis in place of hydrogen sulphide, 73
- Tauber, E., and R. Norman, "Die Derivate des Naphthalins welche für die Technik Interesse, besitzen übersichtlich zusammengestellt" (review), 72
- Taylor, R. L., "Exercises in Practical Chemistry, mostly Quantitative" (review), 317
- Tea cigarettes, 143
- Technical ammonium sulphate, sulphocyanogen in, 317
and scientific department of the Imperial Institute, 241
College, Bradford, 130
- Technical College, Glasgow and West of Scotland, 135
Institute, Beswick, 138
Swansea, 138
School, Stockport, 138
- Teeth, evolution of, use of X rays for, 295
- Tellurium, Japanese, atomic weight of, 106
determination of by precipitation as the iodide, 189
- Temperatures, high, measurement of, 258
treatise by L. Holborn and W. Wien on, 150
- Terpenes and allied compounds, 252, 279
- Tertiary benzenoid amines, 303
- Tetrachloride, antimony, action of nitrogen peroxide upon, 61
- Tetraiodide, zirconium, 102
- Tetra-nitro-cellulose, 239
- Thallium and diphenyliodonium nitrates, are they isomorphous? 217
- Thalleoquin reaction, 100
- Thermometers, 75
- Thiele, H., atomic weight of cobalt, 110
- Thiocarbimides derived from complex fatty acids, 290
- Thioacetic acid in analysis, 73
- Thionyl chloride, action of certain hydrogen compounds upon, 306
- Thiophen in benzene, 50
- Thiophene, action of aluminium chloride upon benzene containing, 97
- Thomas, E. L., and S. Young, a dephlegmator, 258
- G. L., F. R. Barrell, and S. Young, separation of three liquids by fractionated distillation, 258
- V., absorption of nitric oxide by ferrous bromide, 317
action of iodine upon stannous chloride, 49
nitrogen peroxide upon antimony tetrachloride, 61
- Thompson, S. P., properties of a body having a negative resistance, 8
- Thoms, H., pure ether for narcotising, 81
- Thoria and ceria, separation of, 237
- Thorium nitrates, commercial, 257
separation of from the other rare earths by means of potassium trinitride, 314
- Thorpe, J. F., and W. H. Perkin, condensation of halogen derivatives of fatty ethereal salts with ketones and ketonic acids, 119
- Threlfall, Prof., and Mr. Pollock, experiments with Röntgen's radiation, 254
- Thurmann, H., and Th. Pfeiffer, nitric nitrogen in presence of organic nitrogen, 110
- Tickle, T., W. R. Dunstan, and D. H. Jackson, action of methyl alcohol on aconitine, formation of methyl benzconine, 120
- Tilden, W. A., some products from pinene tetrabromide, 94
action of bromine on pinene, 94
- Tin, action of silicon upon, 73
- Tinstone crystals, 115
- Titanium, separation of tungsten from, 293
- Tobacco, nicotin and ammonia in, 185
- Toluidin and benzidin, 109
- Tommasi, D., electrolytic desilvering argentiferous lead, 37, 40
- Topaz, 116
- Toxines, animal and microbial, 37
- Trades' unionist demands, 193
- Trees, influence of on malaria, 48
- Trichloroacetic acid, solutions of, 85
- Trichloropyrogallol, formation of, 49
- Trimethylamine, separation of from ammonia, 116
- Trimethylenic compounds, 97
- Trinity College, University of Dublin, 125
- Trouton, F. T., duration of X radiation at each spark, 177
- Trouvé, G., on lighting with acetylene, 12
- Truchot, P., "L'Ammoniaque, ses Nouveaux Procédés de Fabrication et ses Applications" (review), 48
- Tschirch, A., and O. Oesterle, colour reactions of saffron and its adulterants, 306
- Tuberculosis in goats, 13
- Tubercles, of leguminous plants, 270
- Tubes, musical, 304
- Tulba Haut, organic matter in the mineral water of, 293
- Tungsten, analytical characters of the compounds of, 18, 97
researches on, 61
separation of from titanium, 293
- Tuttie, H. B., "Chemistry at a Glance" (review), 72
- Twin elements, 211, 224
- Tyrosinase and laccase in the juice of certain fungi, 174
- UFFREDUZZI**, B., reactions of the pigment of bacillus prodigiosus, 62
- Ultra-violet spectrum, absorption of by crystalline substances, 196, 204
- Universities and colleges, 123
- "University College of North Wales, Calendar for 1896-7" (review), 256
- University College, 125
Bristol, 128
Dundee, 134
Liverpool, 130
Nottingham, 133
of Wales, Aberystwyth, 127
of North Wales, Bangor, 127
of South Wales and Monmouthshire, Cardiff, 128
of Aberdeen, 198
of Cambridge, 124
of Dublin, Trinity College, 125
of Edinburgh, 434
Chemical Society, 318
of London, 123
of Oxford, 124
of St. Andrews, 135
Tutorial College, 137
- Uranic rays, various properties of, 305
- Uranium compounds, thermic researches on, 49
salts, action of light on organic acids in the presence of, 55, 67, 79
- Urban, G., condensation products of isobutyric aldehyd, 12
- Uric acid, 25
fermentation of by micro-organisms, 84
in guano, 229
in urine, 318
- Urine, mercury in, 318
reaction for acetacetic acid in, 318
uric acid in, 318
- Urotiline, detection of, 318
- VACUUM** water-bath for temperatures above 100°, 197
- Valenta, E., solubilities of the silver haloids in organic and inorganic solvents, 109
- Vanadic acid, reduction of by hydriodic and hydrobromic acids, 202
- Vanadium carbide and cast vanadium, 11, 29
pentoxide, 38
- Van der Kerk, J., and L. C. Schröder, double compounds of aniline with metallic salts, 185
- Van Ritter, G., zinc in organic salts, 186
- Varet, R., double cyanides, 73
oxy-salts of mercury, 84
double bromides, 196
chlorides, 161
- Vaubel, W., action of nascent bromine upon benzene, 109
behaviour of the naphthols and naphthylamines with nascent bromine, 109
determination of value of naphtholic and naphthylaminic sulpho-acids, 293
valuation of benzidin and toluidin, 109
- Vedrdi, V., nicotin and ammonia in tobacco, 185
- Vegetable and animal oils in mineral oils, 62
- Vegetables in tin boxes, blackening of, 25
- Venable, F. P., and T. Clarke, study of the zirconates, 42, 54
"Development of the Periodic Law" (review), 221
- Veterinary College, Glasgow, 138
- Vicille and Berthelot, MM., explosive properties of acetylene, 209
- Vigoreux, E., action of silicon upon the alkaline metals, zinc, aluminium, lead, tin, antimony, bismuth, gold, and platinum, 73
- Villard, P., combination of argon with water, 122
- Vinegar, mineral acids in organic acids, especially in, 49
- Villari, E., researches on the X rays, 73, 174, 161, 233
- Vinyltrimethylene, 85
- Vielle, M., report on a system of gas-burners devised by A. Bondsept, 12
- Viper, action of the porcelain filter upon the poison of, 12
- Vitali, D., mercury poisoning, 40
- Volhard, J., new apparatus, 25
- "Volumetric Analysis, Systematic Handbook of" (review), 173
- Volumetric determination of hydroxylamine, 293
of iron in the ash of plants and animals, 306
- Von Jonstorff, H. J., standard methods of analysis, 81, 89, 101, 118, 143, 159, 170
- WADELL**, J., permeability of various elements to the Röntgen rays, 298
- Wait, C. E., oxidation of silver, 310
- Walbaum, H., and J. Bertram, oil of reseda root, 74
- Walker, J., and J. R. Appleyard, absorption of dilute acids by silk, 105
and J. Henderson, halogens in organic substances, 49
- J. W., action of formic aldehyd on phenyl hydrazine, and on some hydrazones, 120
- electrolysis of the salts of mon-hydroxy acids, 120
- M. S., use in the chemical laboratory of the electric arc, 92
- Warren, B., elementary analysis with the use of lead chromate, 110
- H. N., an electric blowpipe, 281
manufacture of peroxide of lead, 144
nitrogen absorbent for the liberation of argon, 6
preparation of boron, 64

- Warren, H. N., ice for laboratory use, 197
 tetra-nitro-cellulose, 239
 Water, combination of argon with, 122
 nitrites in, 222
 distilled in copper vessels, oxidising properties of, 197
 examination of, 50
 expansion of on change of temperature, 258
 London, the purity of, 243
 mineral, of Tuiha Haut, organic matter in, 293
 iodine in, 186
 colour of alcohols compared with that of, 181
 potable, chemical and bacteriological examination of, 73
 relations of contraction on mixing acetone with, 293
 supply, London, 41, 88, 169, 207, 266, 313
 taking samples of for bacteriological purposes, 258
 use of phenolphthalein in illustrating the dissociating action of, 32
 Waxes, analysis of, 50
 Weiss, consistency meter, 258
 Westminster College of Chemistry and Pharmacy, 137
 West of Scotland and Glasgow Technical College, 135
 Wharton, F. M., and P. Frankland, position-isomerism and optical activity, 105, 279
 Wheat flours, value of from the baker's point of view, 281
 Wiesbaden Chemical Laboratory, 112
 Wild, W., and C. Engler, separation of ozone from hydrogen peroxide, 180
 Wiley, H. W., cotton seeds, 281
 Wilcox, F. A., and F. W. Jones, analysis of cap composition, 283
 Williams, E. D., "Made in Germany" (review), 148
 Windisch, W., chemical laboratory of the brewer, 50
 Wine, examination of, 110, 197
 Wines, detection of caramel in, 306
 alcohol and extract in, 25
 red, examination of for foreign colouring-matters, 196
 Spanish earth for clarifying, 306
 Winkelmann and Schott, properties of certain new glasses devised by, 12
 Winton, A. L., ammonium molybdate solution, 35
 Wislicenus, H., and H. Kaufmann, aluminium amalgam, 197
 Wolf, C. G. L., and S. Ruhemann, ketonic acids, 252
 "Wood Charcoal, an Inquiry into the Alleged Liability of to Spontaneous Combustion" (review), 61
 Woodward, C. J., Science and Art Department, 196
 Woolcott, G. H., R. Meldola, and E. Wray, chemistry of phenol derivatives, 251
 Wool fat, valuation of, 62
 Wrampelmeyer, E., manurial matter, containing insoluble phosphoric acid, 318
 Wray, E., R. Meldola, and G. H. Woolcott, chemistry of phenol derivatives, 251
 Wright, R. P., C. M. Fleischmann, and C. M. Aikman, "The Book of the Dairy" (review), 173
 Wyruboff, Dr., periodic classification of the elements, 31
 X RAYS, 37, 60, 61, 73, 97, 161, 174, 177, 233, 270, 295, 305
 YEAST, analysis of, 62
 Yellow phosphorus, 318
 Yonne, the Seine, and the Marne, nitric acid in the waters of, 305
 Young, S., F. R. Barrel, and G. L. Thomas, separation of three liquids by fractionated distillation, 258
 and E. L. Thomas, dephlegmator, 258
 Yttria group, earths of the, contained in the monazite sands, 292
 Yttrium, atomic weight of, 62
 ZAY, C. E., and Haselhoff, nitrogen in organic substances, 293
 Zettnow, cleansing port-objects from oil, Canada balsam, &c., 258
 Zinc, action of silicon upon, 73
 on a photographic plate, 61
 in American apple rings, 49
 iron, and nickel, electrolytic determination of, 91
 in organic salts, 186
 solution of in dilute acids, 303
 sulphide, phosphorescent, 149
 Zinciferous galena, 114
 Zirconates, a study of, 42, 54
 Zirconium tetraiodide, 102
 Zircono-tungstic compounds, 12

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